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Report RMD 5043-Q2-65

Contract No. NOnr 4364(00)

(U)

ADVANCED OXIDIZER RESEARCH

Report Period: 1 April 1965 to 30 June 1965

Research reported in this publication was supported by the Advanced Research Projects Agency.

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

Report RMD 5043-Q2-65

Report Period: 1 April 1965 to 30 June 1965

Report Date: 30 June 1965

Contract No. NOnr 4364(00), ARPA Order No. 417, Amendment No. 2

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GENERAL FOREWORD

This quarterly report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer.

This report consists of the three following sections:

Section	Task No.	Title
I	51	Difluoramine Chemistry
II	53	Inorganic Oxidizer Synthesis
III	55	Thermal Stability of Advanced Solid Oxidizers

ABSTRACT

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division directed toward the development of advanced solid oxidizers. The three major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as three separate sections of this report.

SECTION I - DIFLUORAMINE CHEMISTRY

Several potential synthetic routes to cyclohexyldifluoramine have been investigated. The fluorination of cyclohexylisocyanate or of N-cyclohexyl-p-toluenesulfonamide was less satisfactory than the fluorination of ethyl N-cyclohexylcarbamate. Cyclohexyldifluoramine could not be prepared by the acid-catalyzed reaction of cyclohexanol with difluoramine or by the reaction of cyclohexyl iodide with tetrafluorohydrazine.

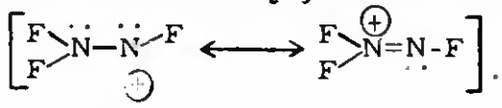
Cyclohexylidenefluorimine was prepared readily by the dehydrofluorination of cyclohexyldifluoramine. The dehydrofluorination of α,α-bis(difluoramino) toluene led to the formation of a second product, believed to be fluorofluoriminotoluene, in addition to the expected trifluoroamidine.

The addition of tetrafluorohydrazine to 2-pentene produced 2,3-bis(difluoramino)pentane in its two diastereoisomeric forms, which were separated chromatographically.

2,2-Bis(difluoramino)phenylethane was synthesized successfully by a two-step method. Difluoramine added to phenylacetaldehyde to give the hydroxydifluoramine, which reacted with additional difluoramine in the presence of acid to yield the desired gem-bis(difluoramine).

SECTION II - INORGANIC OXIDIZER SYNTHESIS

The stoichiometry of the adduct of N_2F_4 with AsF_5 at room temperature has been confirmed to be 1:1. The uptake of AsF_5 by N_2F_4 at -80°C has been shown to produce adducts in which the AsF_5:N_2F_4 ratios are two or greater.

Infrared spectra have been obtained for the N_2F_4-AsF_5 reaction product at -80°C and of the final product at room temperature. The reaction of $N_2F_4 \cdot AsF_5$ with fluoride ion in IF_5 produces trans-N_2F_2 and NF_3 as well as N_2F_4. This is interpreted as chemical evidence that the 1:1 adduct does not have a molecular constitution. The F^{19} n.m.r. spectrum of HF solutions of the 1:1 adduct indicates the presence of three nonequivalent N-F fluorines, which is interpreted as evidence of the existence of an $N_2F_3^+$ cation in which rotation about the N-N bond is restricted  .

Attempts to prepare O_2BrF_5 from $CsBrF_4$ and O_2AsF_6 in a glass system gave $CsAsF_6$, O_2, F_2, Br_2, and SiF_4. The results of attempts to prepare O_2ClF_4 from O_2AsF_6 and $CsClF_4$ are incomplete.

SECTION III - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

A method suitable for preparation of research quantities of high-purity hydroxylammonium perchlorate (HAP) in a reasonaly short time has been developed. Thermal decomposition rate experiments have been performed in the region of 120°-160° and the activation energy of the uncatalyzed reaction found to be 44.3 kcal/mole. In contrast to the $HONH_3Cl$ reaction previously studied, no evidence of competing reactions is shown.

The vaporous products have been identified as N_2O, HCl and Cl_2; ClO_4^-, $HONH_2$ and NH_3 have been found in the highly acidic condensed residue, which is suspected to be a mixture of HAP, NH_4ClO_4 and aqueous $HClO_4$. Experiments designed to discover the stoichiometry of the reaction have been undertaken.

Thiokol
REACTION MOTORS DIVISION

SECTION I

ORGANIC DIFLUORAMINE CHEMISTRY

Harry F. Smith

Report RMD 5043-Q2-65

RMD Project 5043, Task 51
Report Period: 1 April 1965
to 30 June 1965

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 5910

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FOREWORD

This section of the quarterly progress report on advanced oxidizers describes research performed from 1 April 1965 to 30 June 1965 in the synthesis and chemical reactions of organic fluoronitrogen compounds, and on the preparation of selected difluoramino compounds for structure-sensitivity correlation studies.

Technical personnel contributing to this effort were: H. F. Smith (Project Supervisor), J. J. Dvorak, J. A. Castellano, W. H. Wieting and E. St. Cyr (Synthesis), and D. G. Chowanec, J. A. Creatura, D. F. Kates and D. N. Pregler (Analytical Support).

ABSTRACT

Several potential synthetic routes to cyclohexyldifluoramine have been investigated. The fluorination of cyclohexylisocyanate or of N-cyclohexyl-p-toluenesulfonamide was less satisfactory than the fluorination of ethyl N-cyclohexylcarbamate. Cyclohexyldifluoramine could not be prepared by the acid-catalyzed reaction of cyclohexanol with difluoramine or by the reaction of cyclohexyl iodide with tetrafluorohydrazine.

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2,2-Bis(difluoramino)phenylethane was synthesized successfully by a two-step method. Difluoramine added to phenylacetaldehyde to give the hydroxydifluoramine, which reacted with additional difluoramine in the presence of acid to yield the desired gem-bis(difluoramine).

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ILLUSTRATIONS

ILLUSTRATIONS (cont)

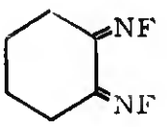
TABLES

I. INTRODUCTION

The research described in this section of the quarterly report has been directed toward two objectives. These are an exploration of the chemistry of organic fluoronitrogen compounds, and the preparation of selected difluoramino compounds for investigation of the relationship between sensitivity and molecular structure.

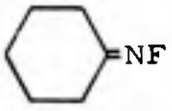
From the broad field of organic fluoronitrogen derivatives we have selected for intensive study the more limited area embracing the preparation and reactions of compounds containing the ketofluorimine group, $>C=NF$. This selection reflects the current importance of perfluoroguanidine, $(NF_2)_2C=NF$, as a molecular building block for new energetic oxidizers. The most promising materials for propellant applications are derived from perfluoroguanidine by addition reactions at the double bond. We hope to contribute significantly to the advance of propellant technology by defining the nature and scope of these addition reactions, by means of an intensive examination of the chemical reactions of analogous compounds containing the ketofluorimine group.

Our initial efforts in this area were directed toward an exploration of the reactions of 1,2-difluoriminocyclohexane, I, the most readily available



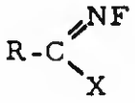
I

model compound (Ref 1, 2). This compound was found to be unreactive with most of the reagent systems examined. As a consequence, the investigation has been extended in two directions. The first represents an attempt to eliminate the possible steric or electronic interference between the two ketofluorimine groups in I, by introducing a simpler model compound, cyclohexylidenefluorimine (II). This model will be employed for an investigation of



II

those reactions which occur with olefins and with ketones. The second new direction involves the use of electronegatively substituted ketofluorimines (III), which represent closer analogs to perfluoroguanidine. Model compounds

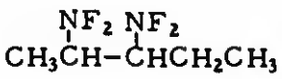


where X = NF_2, OR^1, CF_3, or F

III

of this class are appropriate for the study of the addition reactions which are characteristic of perfluoroguanidine.

This report also contains a description of the progress made in the synthesis and purification of selected difluoramino compounds for investigation of the relationship between sensitivity and molecular structure, and for thermochemical measurements. Major emphasis has been placed upon the preparation and purification of the two diastereoisomeric forms of 2,3-bis(difluoramino)pentane (IV). Significant progress has also been made during the current report period on the synthesis of derivatives of phenylethane and on the preparation of 1,1-bis(difluoramino)heptane (V) in higher purity.



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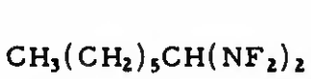
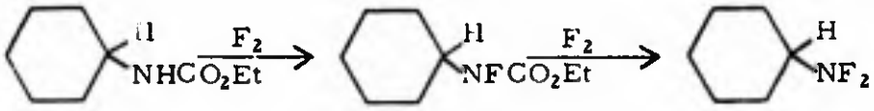


V

II. DISCUSSION

A. SYNTHESIS OF CYCLOHEXYLDIFLUORAMINE

A number of experiments involving the fluorination of ethyl N-cyclohexylcarbamate in a Freon-water emulsion system have been described in an earlier report (Ref 2). The results obtained, although better than fluorination in acetonitrile solution, still left much to be desired in the synthesis of the precursor of a model compound required for reaction studies. The yield of cyclohexyldifluoramine (VI) was limited, in several runs, to 5 to 6% of theory. Small amounts of ethyl N-fluoro-N-cyclohexylcarbamate (VII) were obtained, but



(1)

VII VI

the major portion of the starting material was recovered. The cessation of reaction at this point appeared to be unaffected by the continued introduction of additional fluorine. When the quantity of carbamate used was decreased by one-half without altering the remainder of the reaction mixture, the reaction proceeded until approximately the same quantity of VI had been formed, effectively doubling the yield. This result suggested that a byproduct was inhibiting the reaction after its concentration reached some critical level.

The most obvious of the possible interfering byproducts is the hydrogen fluoride which is known to be liberated during the reaction. An attempt to control this factor by including a stoichiometric quantity of calcium carbonate in the reaction mixture was unsuccessful. No significant quantity of VI was obtained. In a related experiment, the pH of the aqueous system was determined at intervals, and was adjusted with sodium carbonate whenever it was found to have dropped to pH 3 or below. In this case also none of the desired product was obtained. A first attempt to obtain usable quantities by scaling up the system which had given 10% yields was also frustrated. Only traces of VI

were obtained in this experiment, and the principal product was VII. The carbamate used was from a different batch, and the fluorination appears to be sensitive to minor impurities in this starting material. This effect has not been noted before. The results of these carbamate fluorinations are summarized in Table I.

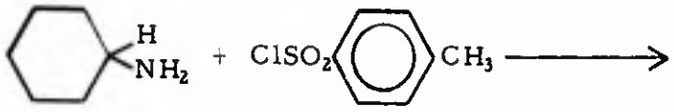
TABLE I

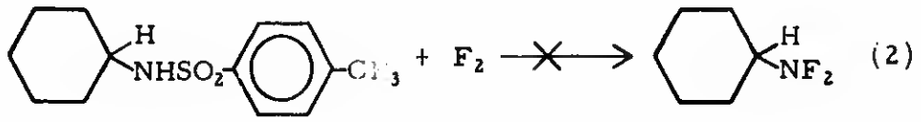
FLUORINATION OF ETHYL N-CYCLOHEXYLCARBAMATE

Experiment No.	Volume[a] (ml.)	Carbamate (moles)	F_2 (moles[c])	pH Control	$C_6H_{11}NF_2$ (moles)	Yield (%)
1	600	0.2	0.6	None	0.011[f]	5.5
2	600	0.1	0.4	None[d]	0.010	10.3
3	600	0.2	0.5	$CaCO_3$[e]	0	0
4	600	0.2[b]	0.5	Na_2CO_3	0	0
5	1200	0.2	1.0	None	0[g]	0

a. Proportions: 515 ml. H_2O, 85 ml. Freon-113, 0.5 g. "Deriphat 151-C" Emulsifier.
b. New batch, apparently less pure.
c. Diluted with N_2 to 20%.
d. Present during reaction 0.2 mole.
e. Added in increments to maintain pH>3.
f. Approximate, corrected for gross impurity.
g. Ethyl N-fluoro-N-cyclohexylcarbamate was the principal product.

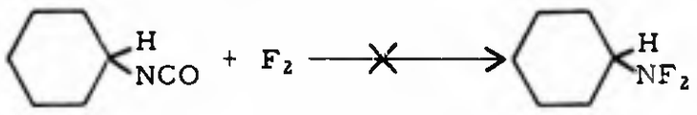
Several attempts were made to synthesize VI by other routes. The fluorination of N-alkylsulfonamides has provided a route to alkyldifluoramines in some instances (Ref 3). N-cyclohexyl-p-toluenesulfonamide was prepared by the reaction of p-toluenesulfonyl chloride with cyclohexylamine. The amide failed to react with 20% fluorine in aqueous suspension at 5 to 10°, and was recovered quantitatively.





VI

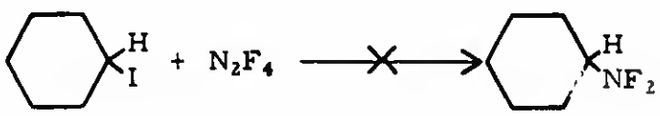
The reaction of cyclohexylisocyanate with 20% fluorine, in Freon-113 solution, produced a yellow liquid product. Its infrared spectrum indicated the



VI

presence of C-F bonds and no more than a trace of N-F. This approach was abandoned as a practical route to the desired intermediate.

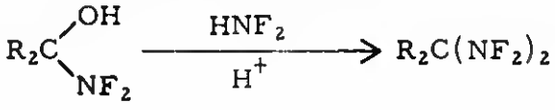
Attempts to utilize the NF_2 free radicals from tetrafluorohydrazine were also unsuccessful. At 70°, N_2F_4 failed to react with cyclohexyl iodide in Freon-113 solution, and 82.5% of the iodide was recovered after 6 hr. Upon increasing the temperature to 110° and the reaction time to 15 hr., some decomposition occurred. Only 33% of the starting material could be recovered, but no N-F containing product was found.



VI

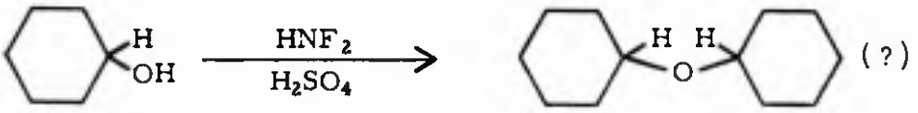
In certain secondary alcohols having an electronegative substituent on the α-carbon (Ref 4, 5), the hydroxyl group has been replaced by NF_2 under

strong acid conditions. One attempt has been made to apply this procedure to the conversion of cyclohexanol to VI. A Freon-113 solution of the alcohol was



$$R_2C(OH)(NF_2) \xrightarrow[H^+]{HNF_2} R_2C(NF_2)_2 \qquad (5)$$

added to difluoramine refluxing at 0 to 5° over fuming sulfuric acid. The oily product obtained was not characterized except to determine that it contained no N-F linkages; it was probably dicyclohexyl ether.

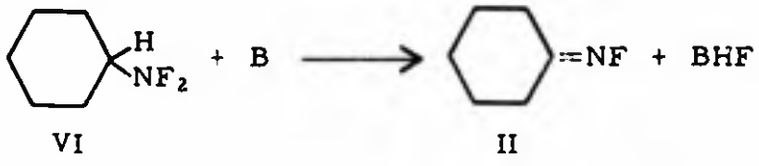


$$\text{cyclohexanol} \xrightarrow[H_2SO_4]{HNF_2} \text{dicyclohexyl ether (?)} \qquad (6)$$

Despite the low yields obtained, the fluorination of ethyl N-cyclohexylcarbamate appears to be the best available route to cyclohexyldifluoramine. Future efforts will be directed toward scaling up this process, using carefully purified carbamate.

B. DEHYDROFLUORINATION REACTIONS

From the experiments described above, sufficient cyclohexyldifluoramine (VI) was obtained for further study of its dehydrofluorination reaction. As we reported earlier, VI was not dehydrofluorinated to any significant extent by reaction at room temperature with either basic ion-exchange resin (Ref 1) or ethyldiisopropylamine (Ref 2). We can now report that VI was effectively dehydrofluorinated by refluxing with the ion-exchange resin in ethyl ether. The fluorimine (II) was obtained in 87% crude yield and identified, after distillation, by its infrared (Figure 1) and F^{19} n.m.r. absorptions.



$$\underset{\text{VI}}{\text{cyclohexyl-NF}_2} + B \longrightarrow \underset{\text{II}}{\text{cyclohexylidene-NF}} + BHF \qquad (7)$$

In view of the difficulty encountered (Ref 6, 7) in obtaining N,N,N'-trifluoroheptanamidine (VIII) by the dehydrofluorination of 1,1-bis(difluoramino)heptane (V), our attention was turned toward the synthesis of an

$$C_6H_{13}CH(NF_2)_2 + \text{Base} \longrightarrow\!\!\!\!\!\!\times\!\!\!\!\!\!\longrightarrow C_6H_{13}C(=NF)NF_2 \qquad (8)$$

V VIII

alternate amidine model compound. N,N,N'-trifluorophenylformamidine, $\phi C(=NF)NF_2$, (IX) was selected for this purpose. In addition to the ready availability of the necessary starting material (X), (the infrared

$$\phi CHO + HNF_2 \xrightarrow{H_2SO_4} \underset{X}{\phi CH(NF_2)_2} + H_2O \qquad (9)$$

spectrum is shown in Figure 2), the phenyl group on the α-carbon provides an additional electronic influence which makes IX an appropriate analog of perfluoroguanidine. In a preliminary experiment, a small quantity of X was dehydrofluorinated by refluxing in methylene chloride with a weakly basic ion-exchange resin. The infrared spectrum of the product, containing absorption peaks at 1642, 1568 and 1555 $cm.^{-1}$ and showing significant changes in the N-F region, 1010 to 800 $cm.^{-1}$, indicated that the formamidine (IX) had been produced.

$$\underset{X}{\phi CH(NF_2)_2} \xrightarrow{\text{Base}} \underset{IX}{\phi C(=NF)NF_2} \qquad (10)$$

When the reaction was repeated on a larger scale, distillation of the crude reaction mixture gave a 16% yield of pale yellow liquid, b.p. 54-57° (6 mm.). Elemental analysis did not agree with the composition of IX, however, and v.p.c. revealed the presence of a second component. Two fractions were separated by preparative scale v.p.c. and the material having the longer retention time was identified by infrared (Figure 3) and n.m.r. (Figures 4 and

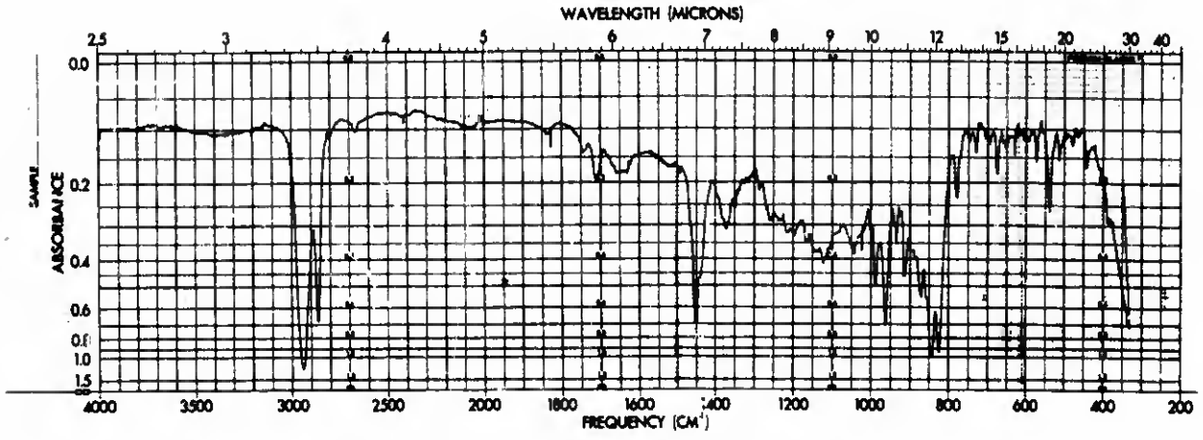


Figure 1. Infrared Spectrum of Cyclohexylidenefluorimine

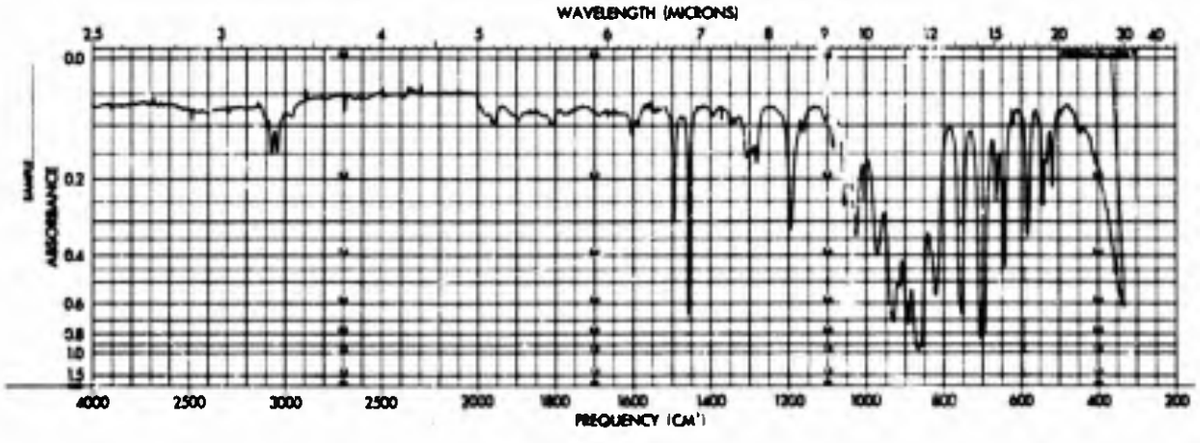


Figure 2. Infrared Spectrum of α,α-Bis(difluoramino)toluene

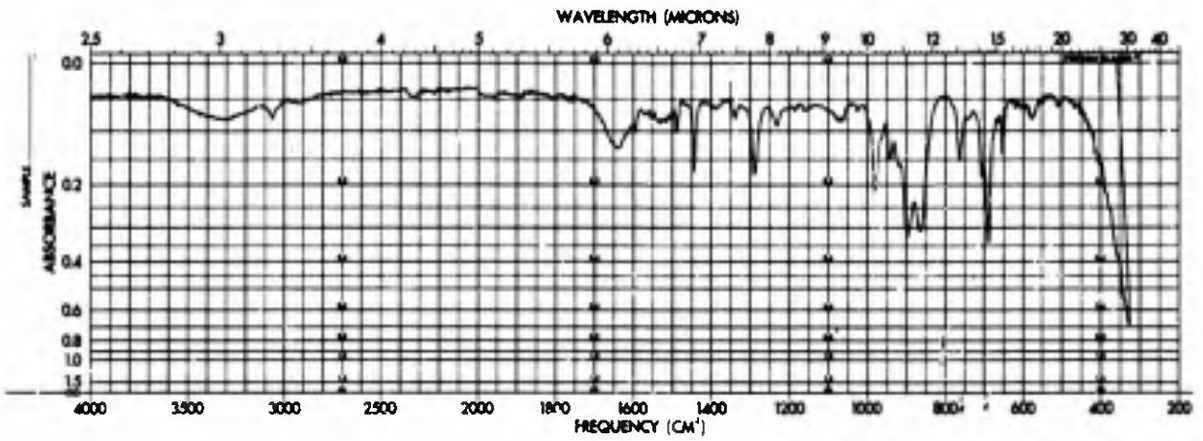


Figure 3. Infrared Spectrum of N,N,N'-Trifluorophenylformamidine

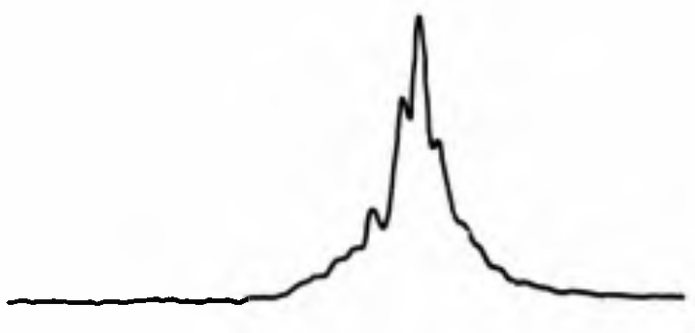
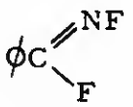


Figure 4. Proton n.m.r. Spectrum of N,N,N'-Trifluorophenylformamidine

5) spectrometry as the formamidine IX. Unequivocal identification of the second component has not been possible. Its infrared spectrum (Figure 6) contained absorptions at 1568 and 1555 cm.$^{-1}$ (C=N), at 1160 cm.$^{-1}$ $\left(F\diagdown C=\right)$ and at 910 cm.$^{-1}$ (=NF). The structure XI is tentatively suggested as the most probable. This dehydrofluorination reaction has been repeated several more times, and an effort to separate the two products by distillation is presently being made. N.m.r. will be employed to confirm the structure of XI.



XI

C. SYNTHESIS AND PURIFICATION OF 2, 3-BIS(DIFLUORAMINO)PENTANE ISOMERS

The title compound (IV) was synthesized by the addition of tetrafluorohydrazine to pentene-2. Since two dissimilar assymetric carbon atoms are present in the product, two diastereoisomeric forms, each of them in turn consisting of a racemic mixture, are possible. As will be seen from the discussion which follows, both forms are in fact obtained, and in roughly equal quantities.

$$CH_3CH{=}CHCH_2CH_3 \xrightarrow{N_2F_4} CH_3CH(NF_2)CH(NF_2)CH_2CH_3 \qquad (11)$$

IV

The crude liquid product was distilled to give three fractions boiling over the range 48 to 50°, 51 to 52°, and 54 to 55°, at 51 mm. Each of these fractions was separable at 60°on a column packed with 20% SF-96 Silicone on A. W. Chromosorb P, into two components, designated α and β, with α having the shorter retention time. As illustrated schematically in Figure 7, the relative amount of α present decreased as the boiling range increased. The measured boiling points of the two isomers, 119° for α- and 123° for β-, are in accord with this observation.

From 30.4 g. of crude adduct there was obtained 4.5 g. of α- and 6.1 g. β-2, 3-bis(difluoramino)pentane of > 99% purity. The infrared spectra, Figures 8 and 9, respectively, are very similar and contain the expected absorptions. These spectra also agree with the infrared spectrum of a sample of IX (mixed isomers) synthesized earlier (Ref 8).

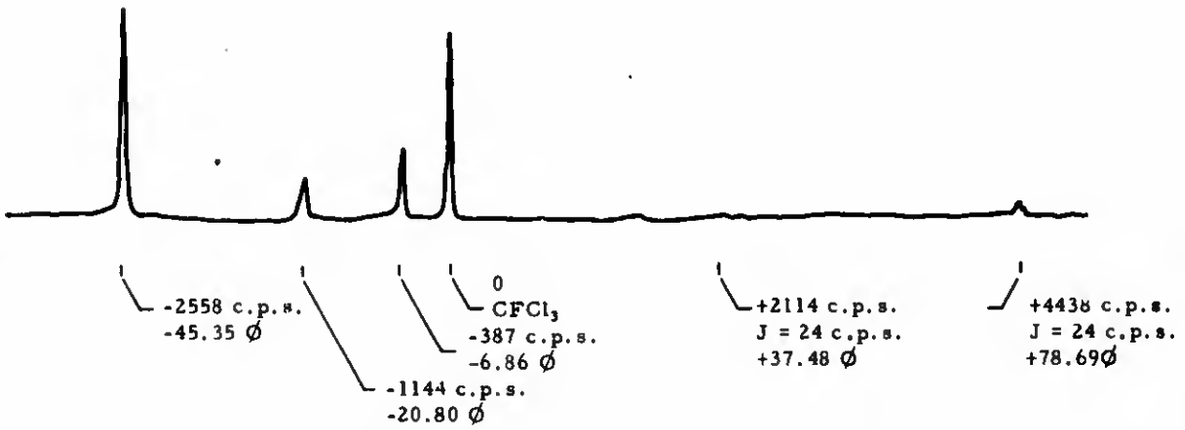


Figure 5. F^{19} n.m.r. Spectrum of N,N,N'-Trifluorophenylformamidine

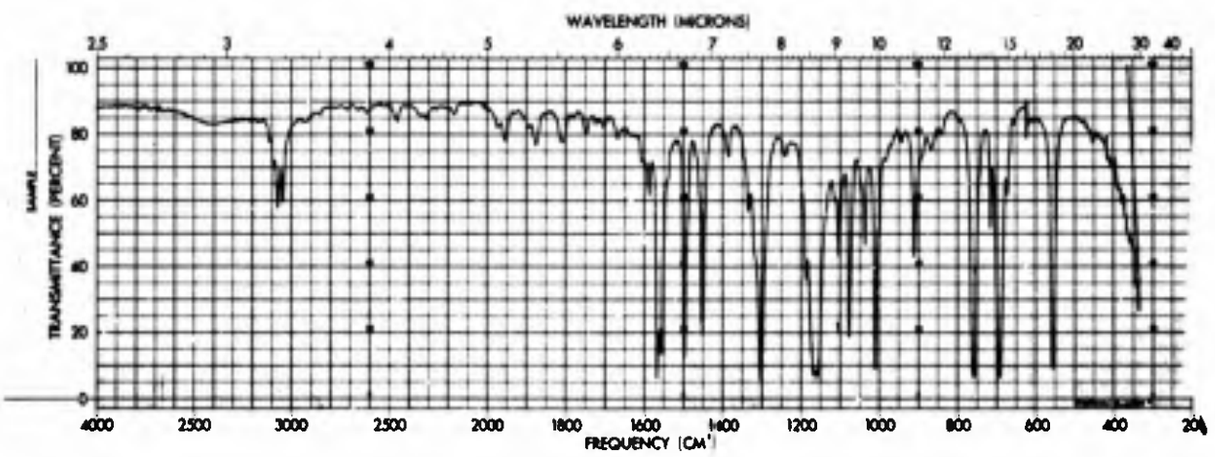


Figure 6. Infrared Spectrum of the Second Product Obtained in the Dehydrofluorination of α,α-Bis(difluoramino)toluene

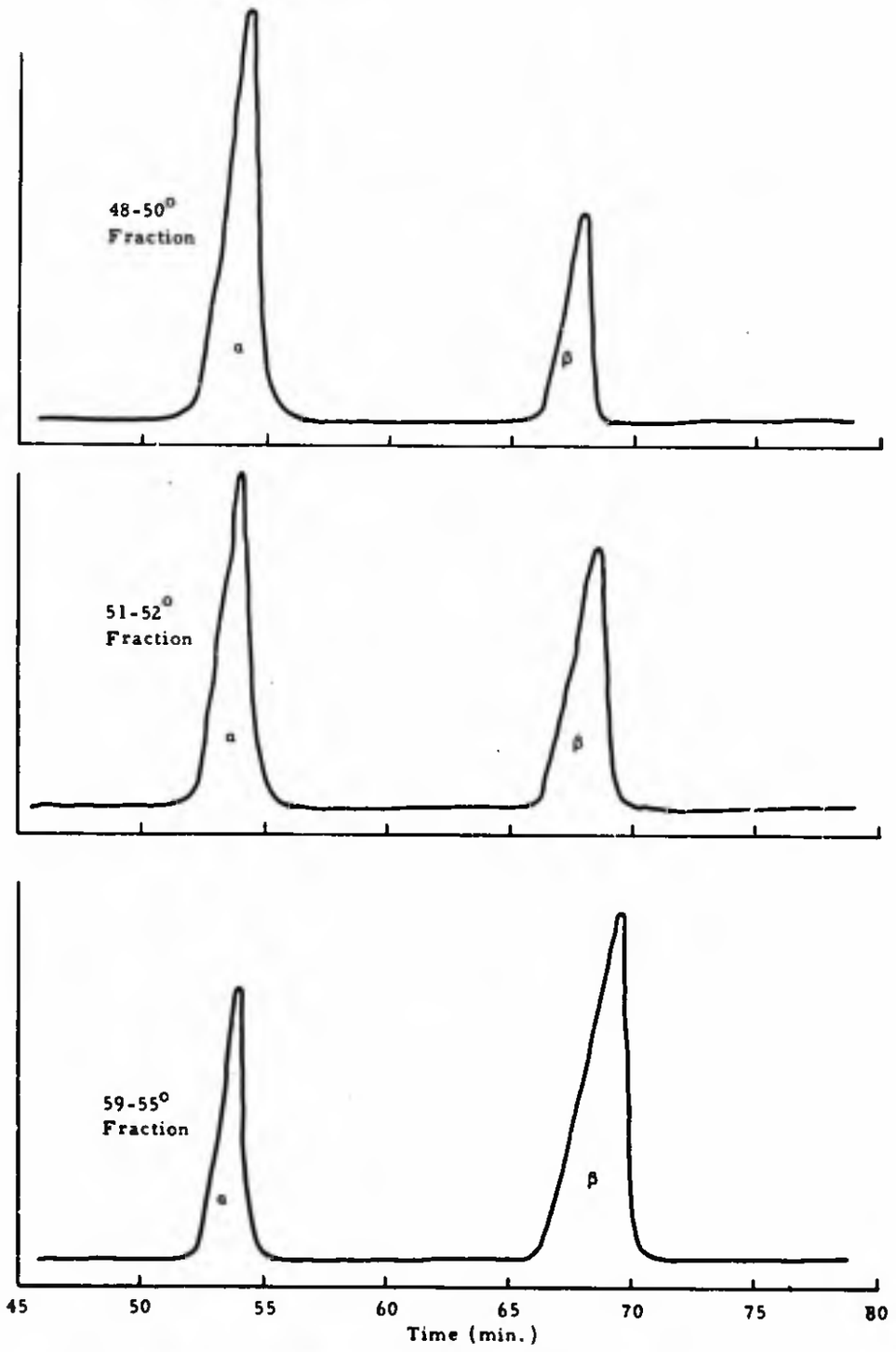


Figure 7. Schematic Representation of v.p.c. Separation of 2,3-Bis (difluoramino) pentane Isomers

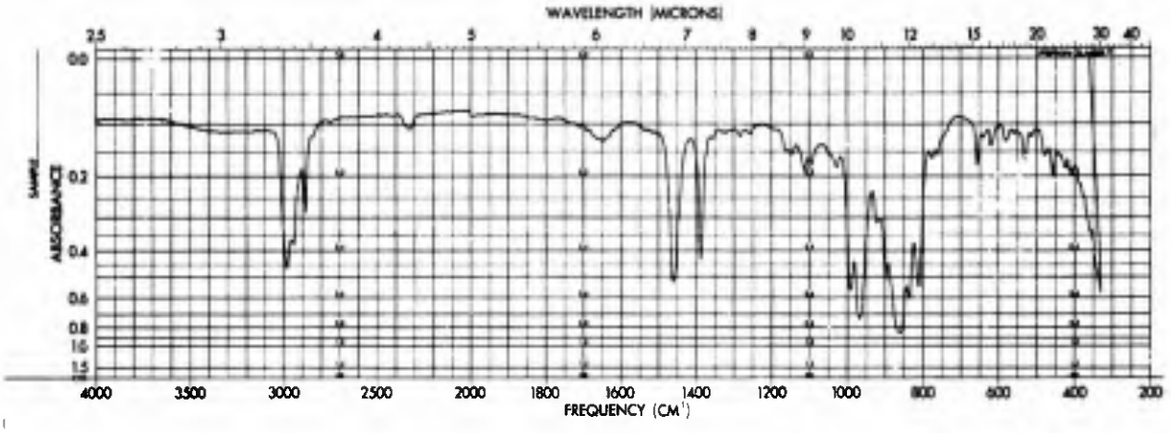


Figure 8. Infrared Spectrum of α-2,3-Bis(difluoramino)pentane

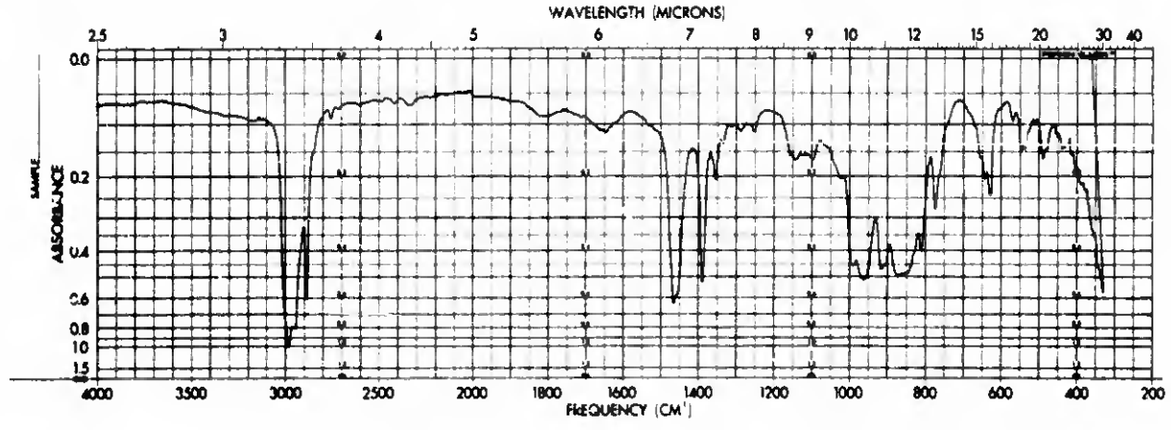


Figure 9. Infrared Spectrum of β-2,3-Bis(difluoramino)pentane

The F^{19} n.m.r. and proton spectra of the α and β isomers provide some interesting information, and permit a tentative assignment of structure. The F^{19} n.m.r. spectrum of the α-dl pair is shown in Figure 10 and is readily decomposed into two large unsymmetrical AB quartets, both further split by coupling to the gem hydrogens to form two eight-line ABX patterns. The central lines of one ABX group overlap to form a triplet. The chemical shifts of the fluorines in this NF_2 group are -40.93ϕ and -37.81ϕ. Coupling constants are J_{FF} = 584 c.p.s. with one J_{HF} = 27.6 c.p.s. and the other J_{HF} = 24.1 c.p.s. The chemical shifts of the fluorines in the NF_2 group belonging to the large central quartet are -43.80ϕ and -39.03ϕ. Coupling constants are J_{FF} = 580 c.p.s., one J_{HF} = 25.3 c.p.s. and the other J_{HF} = 24.8 c.p.s. No assignment of the NF_2 groups to positions on the carbon chain was possible.

The F^{19} n.m.r. spectrum of the β-dl pair is shown in Figure 11, and despite the smaller number of lines observed than in the α-isomer spectrum, it represents a much more complex case. The central lines of the ABX pattern from the fluorines of one NF_2 group may overlap to form a large doublet, dropping the intensity of the outer lines to zero. However, this cannot explain the unusual pattern of the outer lines. It is probable that the spectra of the NF_2 groups cannot be treated independently since there is fluorine-fluorine coupling between the NF_2 groups via the "through space" mechanism (Ref 9, 10). Figure 2 of Reference 9 predicts a J_{FF} of about 20 c.p.s. at an internuclear distance of 2.65Å. Due to the relatively small chemical shift differences, a coupling constant of this magnitude could produce the observed spectrum. Exact chemical shifts and coupling constants can only be obtained from a full theoretical analysis of the spectrum.

The H^1 spectrum of α is shown in Figure 12. The gem protons form a complex multiplet centered approximately at 3.94δ. The C_1-methyl appears as a slightly distorted doublet at 1.36δ with J_{HH} = 7.1 c.p.s. The ethyl group forms an A_3B_2 pattern with the methyl proton appearing as a distorted triplet centered at 110δ and the methylene protons centered at 1.83δ. The latter probably appears as a distorted quintet due to equal coupling constants between the CH_2 protons and the CH_3 protons and the CH_2 protons with the gem proton. The H^1 spectrum of the β-dl pair is shown in Figure 13. The gem protons form a highly complex pattern centered approximately at 3.67δ. The methyl protons of C_1 appear as a doublet centered at 139δ with J_{HH} = 6.9 c.p.s. The ethyl group again appears as an A_3B_2 with the center of the distorted methyl triplet at 1.09δ and the methylene multiplet centered at about 1.85δ.

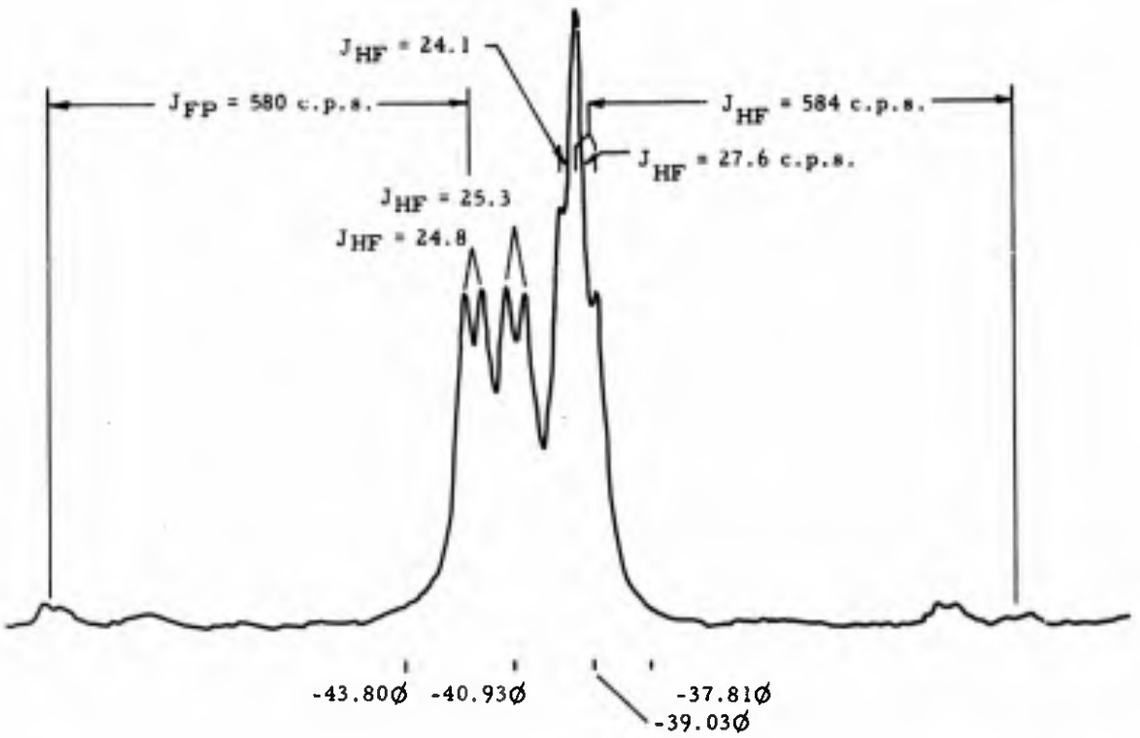


Figure 10. F^{19} n.m.r. Spectrum of α-2,3-Bis(difluoramino)pentane

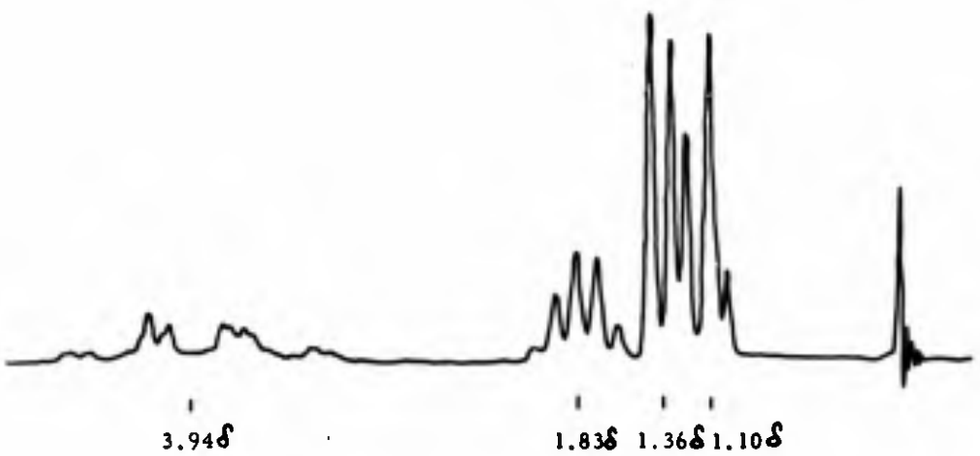


Figure 11. F^{19} n.m.r. Spectrum of β-2,3-Bis(difluoramino)pentane

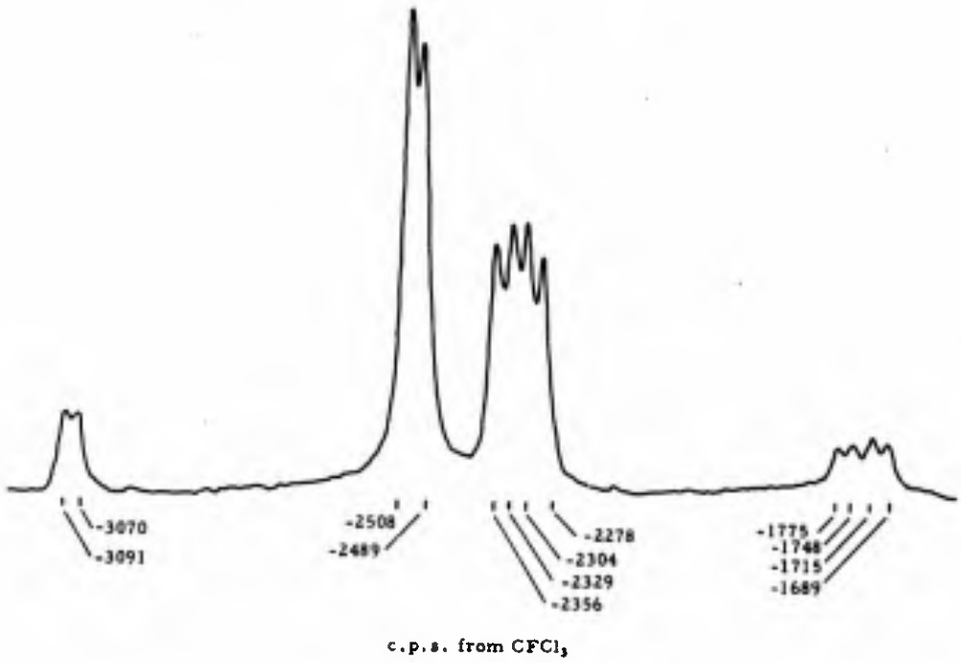


Figure 12. Proton n.m.r. Spectrum of α-2,3-Bis(difluoramino)pentane

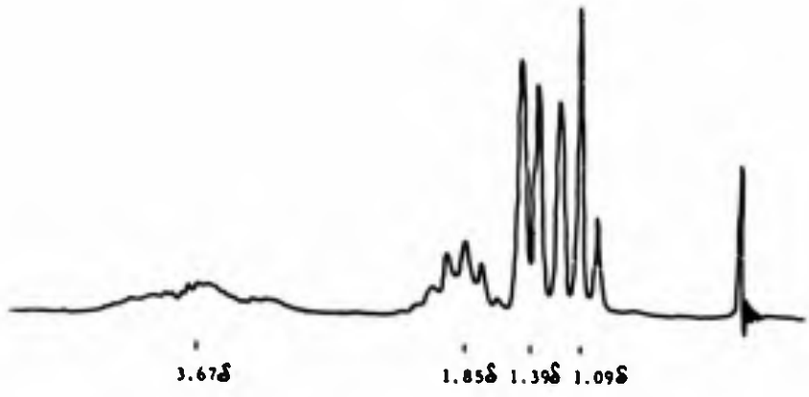
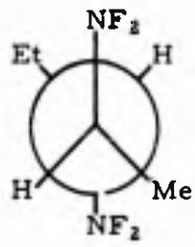


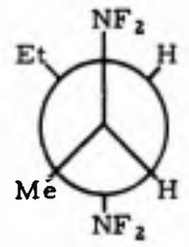
Figure 13. Proton n.m.r. Spectrum of β-2,3-Bis(difluoramino)pentane

The two pairs of enantiomorphs which constitute 2,3-bis(difluoramino) pentane can be represented, each in one of its possible staggered conformations, by the Newman projections (Ref 11) below:

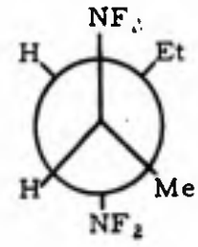
IV D



IV E



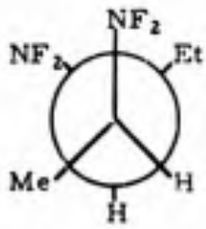
IV F



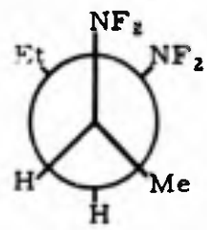
IV G

The view is along the line of the bond between C_2 and C_3. C_2, nearer the observer, is indicated by the radii spaced at 120° angles. C_3, farther from the eye, is designated by the circle with radial extensions.

IV D and IV E, a mirror-image pair, are probably in their most stable conformations as shown, since it is possible for both the difluoramino groups and the alkyl groups to be in the preferred trans positions with respect to each other. In the other pair, IV F and IV G, a trans relationship between difluoramino groups requires a gauche conformation between the methyl and ethyl groups. The same two enantiomorphs can also be drawn as below, with trans alkyl groups and gauche difluoramino groups. It is possible that



IV F^1



IV G^1

this conformation, which brings the fluorine atoms into close enough juxtaposition for through-space coupling to occur, would be favored. For this reason we tentatively suggest that the racemic mixture of IV D and IV E constitutes the isomer we have designated α, while β consists of the racemic mixture of IV F and IV G with the preferred conformations as represented by IV F^1 and IV G^1.

Purified samples of the α- and β-isomers are presently being subjected to a stability test. Any decomposition occurring during storage in the dark at 23-28° in an air atmosphere will be detected by periodic v.p.c. analysis. If no change is detected in one month, required quantities of the two compounds will be submitted to the Naval Ordnance Laboratory for sensitivity testing.

D. SYNTHESIS AND PURIFICATION OF 1, 1-BIS(DIFLUORAMINO)-HEPTANE (V)

The sample of Compound V prepared for thermochemical studies at the Bureau of Mines (Ref 8) was returned to us for further purification. After treatment with sulfuric acid (Ref 2) to remove the carbonyl contaminant (1.0 to 1.5%), the material was apparently not pure, as evidenced by v.p.c. on a Silicone SF-96 column. The reappearance of the same contaminants, when a v.p.c. cut of the principal component was rechromatographed on the same column, implied that decomposition was occurring during chromatography. Decreasing injector temperature had no effect on results; the decomposition probably occurred in the detector.

Additional V was synthesized by the reaction of heptanal with difluoramine under the usual conditions. The combined products from several runs were washed, in Freon-113 solution, with concentrated sulfuric acid and then with water. The dried solution was stripped of solvent and distilled (b.p. 48°/4.5 mm.) to yield 38.7% of V. The infrared spectrum (Figure 14) showed complete freedom from carbonyl contamination, and no impurity could be detected by v.p.c. on a column containing Halocarbon oil on Fluoropak.

E. SYNTHESIS OF 2, 2-BIS(DIFLUORAMINO)PHENYLETHANE (XII)

Initial attempts (Ref 2) to synthesize XII by the classic acid-catalyzed reaction of difluoramine with phenylacetaldehyde (XIII) led to complete degradation of the XIII or, when the amount of acid was decreased, to the formation of the ether (XIV)

$$\underset{\text{XIII}}{\text{ØCH}_2\text{CHO}} \quad \text{HNF}_2 \xrightarrow{H^+} \underset{\text{XIV}}{(\text{OCH}_2\overset{\text{NF}_2}{\overset{|}{\text{C}}}\text{H}-)_2\text{O}} + \text{H}_2\text{O} \qquad (13)$$

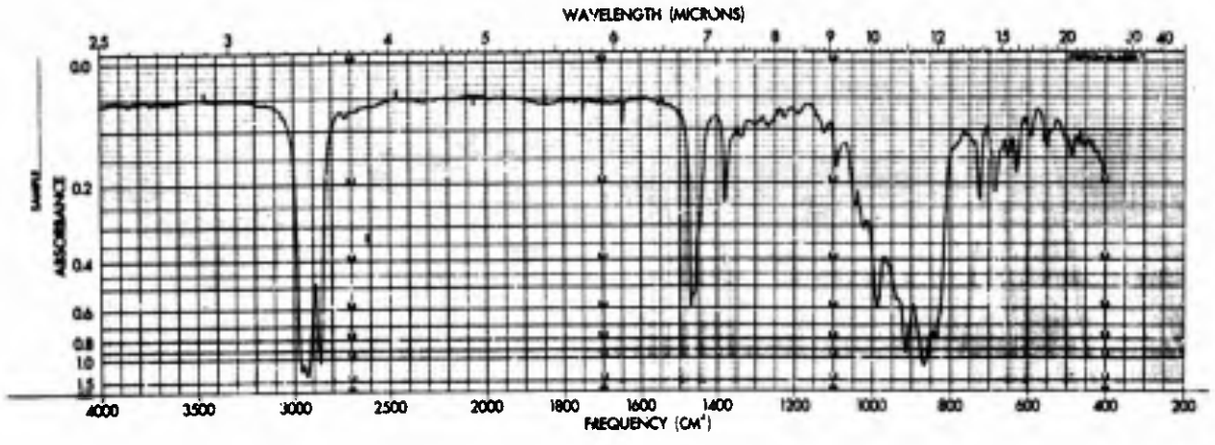


Figure 14. Infrared Spectrum of 1, 1-Bis(difluoramino)heptane

We have now found that the intermediate hydroxydifluoramine (XV) can be synthesized readily by the reaction of XIII with refluxing difluoramine in the absence of acid. The distilled liquid product, b.p. 76° (0.3 mm.), obtained in 52% yield, was identified by means of its infrared spectrum (Figure

$$\underset{\text{XIII}}{\text{ØCH}_2\text{CHO}} + \text{HNF}_2 \longrightarrow \underset{\text{XV}}{\text{ØCH}_2\text{CH}(\text{OH})(\text{NF}_2)} \qquad (14)$$

15). This intermediate, upon treatment with additional difluoramine in the presence of fuming sulfuric acid, was converted to the desired gem-bis(difluoramine) (XII) in 29% yield. After distillation, b.p. 48° (1.0 mm.), the

$$\underset{\text{XV}}{\text{ØCH}_2\text{CH}(\text{OH})(\text{NF}_2)} + \text{HNF}_2 \xrightarrow{\text{H}^+} \underset{\text{XII}}{\text{ØCH}_2\text{CH}(\text{NF}_2)_2} \qquad (15)$$

product exhibited the expected infrared absorptions (Figure 16). Attempts to duplicate this latter step have met with only partial success. The process is apparently sensitive to minor changes in the difficultly controlled variables, such as agitation and rate of mixing, and results have been inconsistent. In some instances, the ether (XIV) was obtained in place of the difluoramine (XII). We are presently attempting to overcome this difficulty by the use of a larger excess of difluoramine in the reaction.

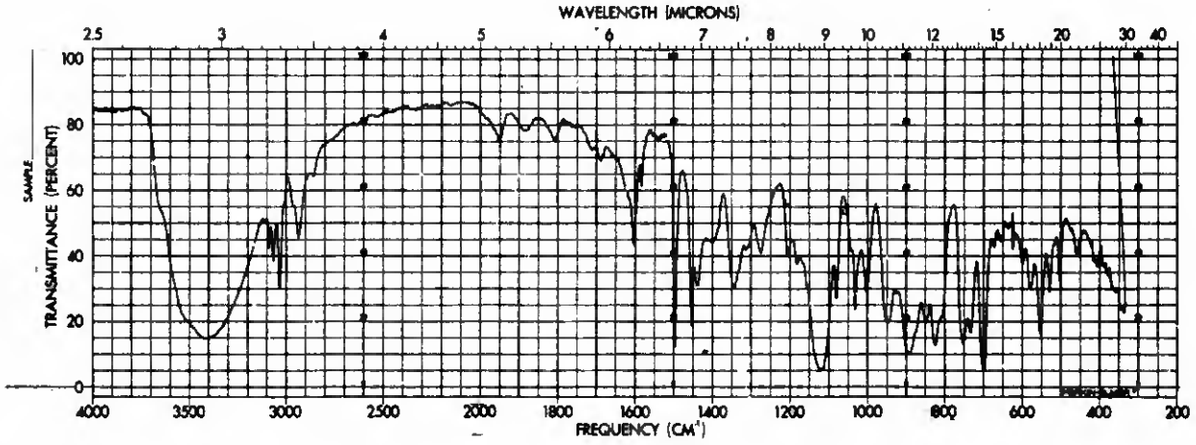


Figure 15. Infrared Spectrum of 1-Difluoramino-2-phenylethanol

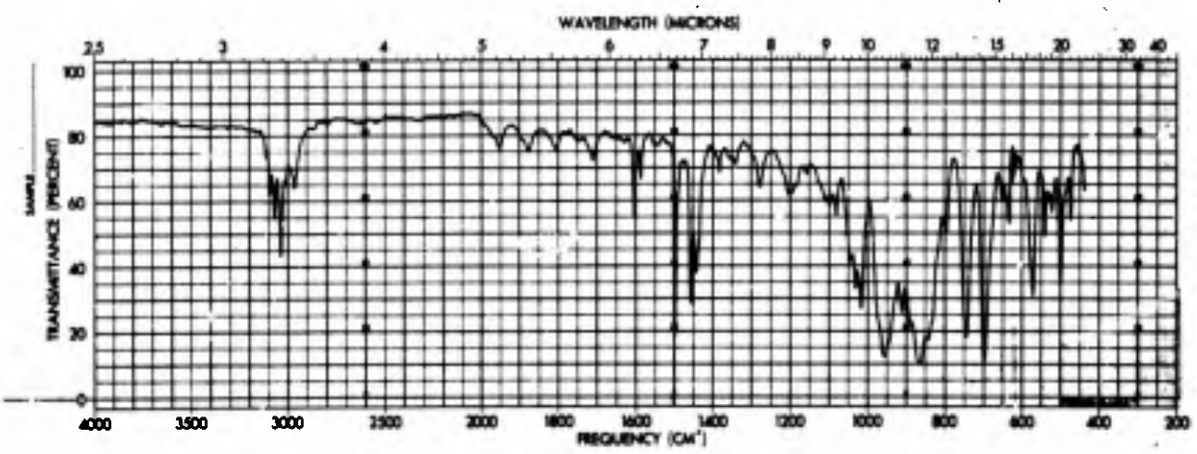


Figure 16. Infrared Spectrum of 2,2-Bis(difluoramino)phenylethane

III. EXPERIMENTAL

A. CYCLOHEXYLDIFLUORAMINE

1. From Ethyl N-Cyclohexylcarbamate

A solution of 17.0 g. (0.1 mole) of recrystallized ethyl N-cyclohexylcarbamate (m.p. 56-57°) in 85 ml. Freon-113 was emulsified in 5.5 ml. water containing ca. 0.5 g. "Deriphat 151C" (General Mills). The mixture was cooled by an external ice bath and held at 0-5° while fluorine, diluted to 20% with nitrogen, was bubbled through. After 8 hr., during which 0.4 mole of fluorine was introduced, consumption of the fluorine ceased. The emulsion broke upon standing without agitation. The solvent layer was combined with two methylene chloride extracts of the acqueous layer, dried, and stripped. The crude liquid product (11.4 g.) was distilled at 24 mm., giving 0.85 g. below 43°, 0.60 g. at 43-56°, and 2.7 g. at 57°. The infrared spectrum of the combined first two fractions contained the absorptions expected for cyclohexyldifluoramine and indicated a small carbonyl contaminant. No N-H absorption was present.

2. From N-Cyclohexyl-p-toluenesulfonamide

p-Toluenesulfonyl chloride (28.5 g., 0.15 mole) was added dropwise to a stirred solution of 6.8 g. (0.168 mole) of sodium hydroxide and 15.0 g. (0.15 mole) cyclohexylamine in 200 ml. water (Ref 12). After the addition was completed, the mixture was heated briefly and acidified with dilute hydrochloric acid. The solid product was collected on a filter and dried. Crude yield was 33.85 g. (89%), m.p. 62-63°. After one crystallization from ethanol, a sample melted at 86-87° (lit. m.p. 87°, Ref 13).

A suspension of 4.7 g. (18.6 mmoles) of recrystallized N-cyclohexyl-p-toluenesulfonamide in 600 ml. water was treated, at 0-5°, with 0.4 mole of 20% fluorine during 16 hr. Testing the gas effluent with starch-iodide paper gave no indication that fluorine was being consumed. Infrared analysis of the solid recovered by filtration indicated that no reaction had occurred.

3. From Cyclohexylisocyanate

Through a solution of 11.0 g. (88 mmoles) of cyclohexylisocyanate (Aldrich Chemical Co.) in 40 ml. Freon-113 at 0-5° was passed 0.20 mole fluorine, in the form of a 20% mixture with nitrogen. A brown precipitate which formed was filtered off, and the filtrate was dried and evaporated. The yellow liquid residue (4.7 g.) showed infrared absorptions attributable to C-F (strong), C=O, N=C=O, and at most a trace of N-F.

4. From Cyclohexyl Iodide

A mixture of 10.0 g. (47.5 mmoles) of cyclohexyl iodide (City Chemical Co.) in 20 ml. Freon-113 was placed in a 75 ml. stainless steel cylinder which was then degassed at -78°. Tetrafluorohydrazine (100 mmoles) was then condensed into the cyclinder at -196°. The cylinder was heated, with shaking, to 70° for 6 hr. After the unreacted N_2F_4 was pumped off, the solution was concentrated to yield 8.25 g. (82.5% recovery) of yellow liquid identified as cyclohexyl iodide.

When a second similarly charged cylinder was heated to 110° for 15 hr., only 33% of the starting material was recovered. The remainder was decomposed to unidentified products.

5. From Cyclohexanol

An aqueous solution of difluorourea (300 ml., containing 0.5 mole) was treated with sulfuric acid, and the liberated difluoramine was collected under Dry Ice reflux in a flask containing 5 ml. of 104% fuming sulfuric acid. To this flask was added, during 4 hr., a solution of 4.82 g. (48.2 mmoles) of cyclohexanol in 10 ml. Freon-113. The reaction mixture darkened and a voluminous solid, which melted to an oil at room temperature, appeared. No cyclohexyldifluoramine was produced.

B. CYCLOHEXYLIDENEFLUORIMINE

To a solution of 1.4 g. (10 mmoles) of cyclohexyldifluoramine (b.p. 38°/24 mm.) in 50 ml. ether was added 3.0 g. (15 meq.) of Amberlite IR-45 (Rohm and Haas Co.). The mixture was heated to reflux for 20 hr. and the resin was removed by filtration. Evaporation of solvent from the dried solution left 1.0 g. (84%) of yellow liquid residue, which after distillation (b.p. 75-78°/30 mm.), gave 0.4 g. of colorless product. Its infrared spectrum showed the C=NF linkage at 1670 $cm.^{-1}$ and changes in the N-F region

800-1040 cm.$^{-1}$. The F^{19} n.m.r. spectrum contained peaks at 16.56 and 18.76Ø, indicative of C=NF.

C. N,N,N'-TRIFLUOROPHENYLFORMAMIDINE

Refluxing 5.0 g. (25 mmoles) of α,α-bis(difluoramino)toluene (b.p. 39°/2.2 mm.) with 7.0 g. (35 meq.) of Amberlite IR-45 in 200 ml. methylene chloride gave 3.50 g. (78%) of orange liquid product. This material was chromatographed on a 12 ft. x 3/8 in. column of 20% Halocarbon oil on Fluoropak at 60°. The first fraction, representing 17% of the total and having a retention time of 12 min., gave an infrared spectrum containing absorptions at 1568 and 1555 cm.$^{-1}$ (C=N), 1160 cm.$^{-1}$ (=C$\diagdown\!\!\diagup_{F}$?), and 910 cm.$^{-1}$ (=NF ?). The major fraction, retained for 49 min., was identified by infrared and n.m.r. spectra as N,N,N'-trifluorophenylformamidine.

Anal.	Calcd. for $C_7H_5N_2F_3$:	C, 48.28; H, 2.89; N, 16.09
	Found	: C, 48.74; H, 2.83; N, 14.96

D. 2,3-BIS(DIFLUORAMINO)PENTANE

In a 75 ml. stainless steel cylinder were mixed 3.90 g. (56.5 mmoles) of pentene-2 (Fisher Scientific Co., 99% pure) and 20 ml. Freon-113. To this was added, by condensing at -160°, 134 mmoles (3 l. at 760 mm.) of tetrafluorohydrazine. The mixture was heated with shaking to 80° for 15 hr. The crude products from this and three identical preparations (30.4 g., 78.5%) were combined and distilled. Material boiling in the range 48-52°/51 mm. was diluted with Freon-113 to permit automatic injection and chromatographed on 20% SF-96 Silicone on A. W. Chromosorb P at 60°. The isomers, α (having the shorter retention time) and β, were cleanly separated, but a mechanical malfunction in the collector permitted the α sample to be contaminated with a small amount of β, necessitating a second pass. Final yields were 4.5 g. of α and 6.1 g. of β.

Anal.	Calcd. for $C_5H_9N_2F_4$:	C, 34.48; H, 5.79; N, 16.09
	Found α	: C, 34.60; H, 5.93; N, 15.13
	Found β	: C, 34.88; H, 5.93; N, 15.34
	B.p., α	: 119°/760 mm.
	B.p., β	: 123°/760 mm.
	n_D^{25}, α	: 1.3688
	n_D^{25}, β	: 1.3728

The n.m.r. spectra were obtained on a Varian DP 60 spectrometer that was operated at 56.4 Mc.for fluorine resonance. Compounds were present as 70% by volume solutions in $CFCl_3$ with about 2% TMS added. The spectra were calibrated by the sideband method using $CFCl_3$ and TMS as internal references.

F. 1-DIFLUORAMINO-2-PHENYLETHANOL

Difluoramine (0.25 mole) was generated and collected under Dry Ice reflux as in A.5. above, in a flask containing 10 ml. Freon-113. To this was added, during 4 hr., a solution of 7.7 g. phenylacetaldehyde (K and K Laboratories, distilled at 65°/1.7 mm.) in 10 ml. Freon-113. The reaction mixture was then warmed to room temperature to remove excess difluoramine. A portion, approximately 67%, was stripped of solvent, and distilled (b.p. 76°/0.3 mm.) to yield 5.75 g. of liquid.

Anal. Calcd. for $C_8H_9NF_2O$: C, 55.49; H, 5.24; N, 8.09
Found : C, 55.54; H, 5.24; N, 7.78

F. 2,2-BIS(DIFLUORAMINO)PHENYLETHANE

A solution of 5.75 g. (33.3 mmoles) of 1-difluoramino-2-phenylethanol in 15 ml. Freon-113 was added during 4 hr. to 0.25 mole of difluoramine refluxing over 4.0 ml., 104% fuming sulfuric acid and 10 ml. Freon-113. After workup as described above, a crude yield of 2.0 g. (29%) of liquid product, b.p. 48° (1.0 mm.) was obtained. The infrared spectrum contained the expected absorption bands for a monosubstituted aromatic compound with NF_2 groups. Elemental analysis was deferred until additional material has been prepared.

IV. FUTURE WORK

During the next quarter our research effort will be devoted to the following areas:

- Preparation of sufficient quantities of the model compounds, cyclohexylidenefluorimine (II), and N,N,N'-trifluorophenylformamidine (IX).
- Exploration of the reactions of II with olefin and carbonyl reagents.
- Study of reactions of the α-carbon in II.
- Exploration of the addition reactions of IX, analogous to those of perfluoroguanidine.
- Preparation of a fluoramino-bis(difluoramino)methoxylalkane, and study of its stability and chemical reactions.
- Purification of 1,1-bis(difluoramino)phenylethane for sensitivity studies.
- Continued synthesis of 2,2-bis(difluoramino)phenylethane.

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Thiokol
REACTION MOTORS DIVISION

SECTION II

INORGANIC OXIDIZER SYNTHESIS

D. Moy
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Report RMD 5043-Q2-65

RMD Project 5043, Task 53
Report Period: 1 April 1965
to 30 June 1965

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 5910

FOREWORD

This section of the report summarizes the results of studies of the synthesis of new inorganic oxidizers during the period from 1 April 1965 to 30 June 1965. This program was monitored by Mr. R. L. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), D. Moy and S. I. Morrow (Principal Investigators) and D. Kates, B. Fagan, G. Rice, D. Yee, and R. Crooker (Analytical).

ABSTRACT

The stoichiometry of the adduct of N_2F_4 with AsF_5 at room temperature has been confirmed to be 1:1. The uptake of AsF_5 by N_2F_4 at -80°C has been shown to produce adducts in which the AsF_5:N_2F_4 ratios are two or greater. Infrared spectra have been obtained for the N_2F_4-AsF_5 reaction product at -80°C and of the final product at room temperature. The reaction of $N_2F_4 \cdot AsF_5$ with fluoride ion in IF_5 produces trans-N_2F_2 and NF_3 as well as N_2F_4. This is interpreted as chemical evidence that the 1:1 adduct does not have a molecular constitution. The F^{19} n.m.r. spectrum of HF solutions of the 1:1 adduct indicates the presence of three nonequivalent N-F fluorines, which is interpreted as evidence of the existence of an $N_2F_3^+$ cation in which rotation about the N-N bond is restricted $\left[F_2N-\overset{\oplus}{N}F \longleftrightarrow F_2\overset{\oplus}{N}=N-F \right]$.

Attempts to prepare O_2BrF_4 from $CsBrF_4$ and O_2AsF_6 in a glass system gave $CsAsF_6$, O_2, F_2, Br_2, and SiF_4. The results of attempts to prepare O_2ClF_4 from O_2AsF_6 and $CsClF_4$ are incomplete.

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ILLUSTRATIONS

TABLES

I. INTRODUCTION

The objective of this task is the study of reactions of inorganic N-F and O-F compounds as an approach to the synthesis of new solid oxidizers. The primary reagents under examination on this program are dioxygenyl difluoride (O_2F_2), dinitrogen difluoride (N_2F_2), and nitrosyl fluoride (NOF). Previous work with these binary inorganic compounds has led to the discovery of hexafluoroarsenates of the dioxygenyl (O_2^+) ion and the fluorodiazonium (N_2F^+) ion. Therefore, we are now placing major emphasis on efforts to synthesize compounds containing these cations in combination with oxidizing anions such as ClO_4^-, ClF_4^-, and NO_3^-. We also have evidence for believing that an adduct of N_2F_4 with AsF_5 contains the $N_2F_3^+$ cation, so we have added the problems of completing the characterization and studying the chemistry of this N_2F_4 derivative to our program.

II. DISCUSSION

A. INORGANIC N-F CHEMISTRY

Past efforts on this program resulted in the synthesis and characterization of a new cation, FN_2^+, and a major objective of this program is to make energetic oxidizer salts of this cation. However, the synthesis of the FN_2^+ cation utilizes cis-N_2F_2 as a starting reagent and this chemical has not been available commercially during the past year. Our recent efforts to synthesize it using a method prescribed by Hurst, et al. (Ref 1) have been successful, and we now have a supply of N_2FAsF_6 for further synthesis studies.

The major effort during the past quarter was devoted to the characterization of the $N_2F_4 \cdot xAsF_5$ adducts. The stoichiometry of the adduct, which is stable at room temperature, has been determined to be 1:1. It has further been shown that at lower temperatures the $AsF_5:N_2F_4$ ratio in the adducts can be two or greater. All of the available evidence points to an ionic constitution for the room temperature adduct.

• CHEMISTRY OF DIFLUORODIAZINE

1. Preparation of trans-N_2F_2

The preparation of trans-N_2F_2 was carried out successfully using the method developed by Hurst, et al. (Ref 1). In this method, $AlCl_3$ and N_2F_4 are allowed to react at -80°C in a flow system giving trans-N_2F_2 and chlorine as the major products condensable at -196°C. Only traces of NF_3 were found by infrared analysis. Separations were easily effected by trap-to-trap distillation through -160° and -196°C baths. The yield of trans-N_2F_2 (based on the consumption of N_2F_4) was approximately 40% and contained less than 1% NF_3 as the only detectable impurity.

2. Preparation of cis-N_2F_2

The isomerization to cis-N_2F_2 was accomplished by heating trans-N_2F_2 to 75°C overnight in a stainless steel cylinder. Considerably longer heating times (15-20 hours) than those reported by Hurst (1-2 hours) were required

for isomerization. The prolonged heating time resulted in a 10-15% loss of N_2F_2 by thermal decomposition. The final mixtures were estimated to contain better than 90% cis-N_2F_2 by infrared analyses.

3. Preparation of $N_2F^+AsF_6^-$

Fluorodiazonium hexafluoroarsenate was prepared by the usual procedure (Ref 2) from AsF_5 and cis-N_2F_2. Approximately one gram was prepared and stored for future use.

• TETRAFLUOROHYDRAZINE - ARSENIC PENTAFLUORIDE ADDUCT

1. Preparation and Stoichiometry

Previous reports (Ref 3) indicated that at least two distinct adducts are formed between N_2F_4 and AsF_5, depending on the temperature at which the preparation is carried out. At -80°C, N_2F_4 and AsF_5 react (Equation 1) to

$$N_2F_4 + xAsF_5 \xrightarrow{-80^\circ C} N_2F_4(AsF_5)_x \qquad (1)$$

to give a product with $x \geq 2$. On warming to room temperature and pumping, the adduct loses AsF_5 to form a second product (Equation 2) in which $y \cong 1$.

$$N_2F_4(AsF_5)_x \xrightarrow{r.t.} N_2F_4(AsF_5)_y + (x-y)AsF_5 \qquad (2)$$

If the preparations are carried out at room temperature, variable results are obtained. The variations in results are no doubt due to: (1) extensive side reactions of N_2F_4 and glass at room temperature in the presence of AsF_5, and (2) concurrent formation of both adducts. X-ray data presented in the previous quarterly report show that the adduct is converted to $NOAsF_6$ on storage in glass at room temperature (Ref 3).

Preparative data gathered during the past quarter confirm these results. Using initial mole ratios of 4:1 (AsF_5:N_2F_4) and a reaction temperature of -80°C, the results shown in Table I were obtained. On warming the solid to room temperature under continued pumping for several hours, the data recorded in Table II were obtained.

TABLE I

REACTION OF N_2F_4 AND AsF_5 AT -80°C

	Initial Reagents (mmole)		Recovered at -80°C		Consumed at -80°C		
Run No.	N_2F_4	AsF_5	N_2F_4	AsF_5	N_2F_4	AsF_5	AsF_5/N_2F_4
1	5.9	23.6	0	10.4	5.9	13.2	2.25
2	1.4	5.6	0	2.4	1.4	3.2	2.29

TABLE II

STOICHIOMETRY OF $N_2F_4 \cdot AsF_5$ ADDUCT AT ROOM TEMPERATURE

	Initial Reagents (mmole)		Recovered at -80°C + ambient		Consumed at -80°C		
Run No.	N_2F_4	AsF_5	N_2F_4	AsF_5	N_2F_4	AsF_5	AsF_5/N_2F_4
1	5.9	23.6	0	18.2	5.9	5.4	0.92
2	1.4	5.6	0	4.0	1.4	1.6	1.14

The preparative data presented in Tables I and II are entirely consistent with the formulation proposed previously (Ref 3). At -80°C, the reaction proceeds smoothly to yield a product containing 2-3 moles of AsF_5 per mole of N_2F_4. On warming to room temperature with continued removal of volatile constituents, AsF_5 is released and the adduct eventually reaches a composition of one mole of AsF_5 per mole of N_2F_4. As yet, however, reliable analytical

data to sustantiate these formulations have not been obtained. Arsenic analyses for the room temperature adduct (Ref 3) indicate an N_2F_4:AsF_5 mole ratio between 1:1 and 1:1.5, with considerable scatter in the results. Likewise, a total nitrogen determination for the room temperature adduct (by the reaction with water (Ref 3) and during this quarter by reaction with NaF in IF_5) gives values for N_2F_4:AsF_5 ranging between 1:1 and 1:1.5. However, the nitrogen determination cannot be accepted with confidence because of the complexities of the reaction of the adduct with water or NaF.

2. Infrared Spectra

Improved infrared spectra were obtained by forming the adduct directly on a silver chloride plate. Spectra were recorded at both -80°C and at room temperature. The adduct was formed by condensing AsF_5 and N_2F_4 directly onto the silver chloride plate at -196°C, warming to -80°C and, eventually, to room temperature. It is significant to note that neither AsF_5 nor N_2F_4, alone, could be maintained as condensates on the silver chloride plate at -80°C.

This spectrum at -80°C agrees qualitatively with those reported previously (Ref 3). The latter were spectra obtained at room temperature by squeezing the powder between silver chloride plates or by mulling it in SbF_5. Notably, the absorption at 700 cm^{-1} (ascribed to AsF_6^-) and the weaker absorption at 1280-1300 cm^{-1}, 1100-1120 cm^{-1}, and between 900-1000 cm^{-1} (possibly N-F absorptions) appear. In addition, absorptions typical of free N_2F_4 and AsF_5 (900-1000 cm^{-1} and 800 cm^{-1}, respectively) also appear, but diminish on prolonged pumping at -80°C. This spectrum is shown in Figure 1. The band appearing at 1020 cm^{-1} was not observed in the previously reported spectra, and may be due to SiF_4. As the sample was warmed slowly with continual pumping, the AsF_5, N_2F_4 and 1300-1280 cm^{-1} bands completely disappeared while new absorptions appeared at 900, 830, 585 and 560 cm^{-1}. The 700 and 1100-1120 cm^{-1} bands remained essentially unchanged This spectrum is shown in Figure 2. Finally, after prolonged pumping at room temperature, the spectrum recorded in Figure 3 was obtained. The broad absorptions centered at 1100 cm^{-1} (shoulder at 1030 cm^{-1}) and at 700 cm^{-1} persist and the two bands at 900 and 830 cm^{-1} are sharpened.

There are several distinct differences between the spectra of the room temperature adduct recorded here and those reported previously. The latter two were recorded from samples prepared by (1) squeezing the solid between AgCl plates or (2) mulling it in SbF_5. It is very possible that the sample recorded by method (1) was not fully converted to the room temperature adduct,

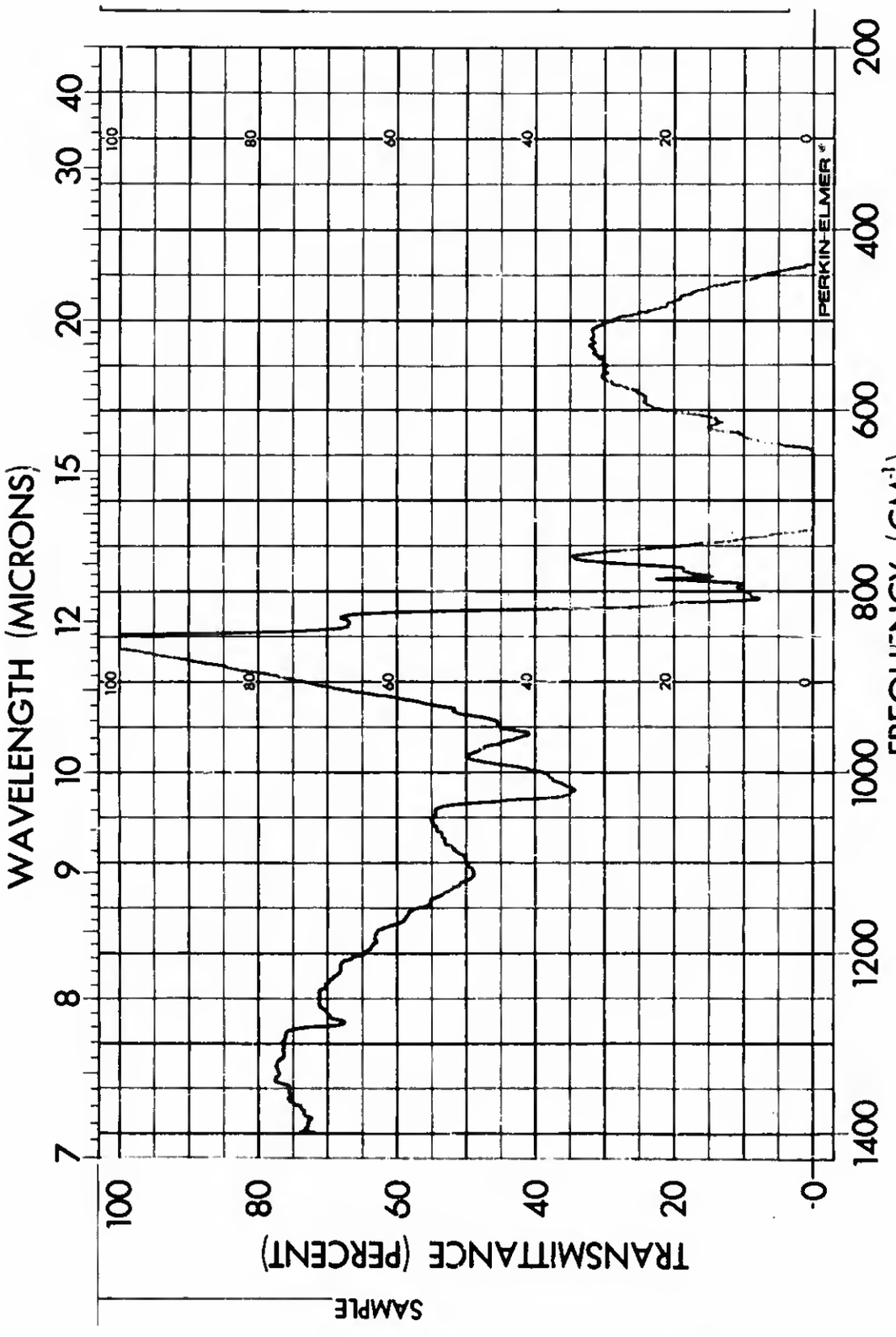


Figure 1. Infrared Spectrum of $N_2F_4(AsF_5)_x$ at -80°C

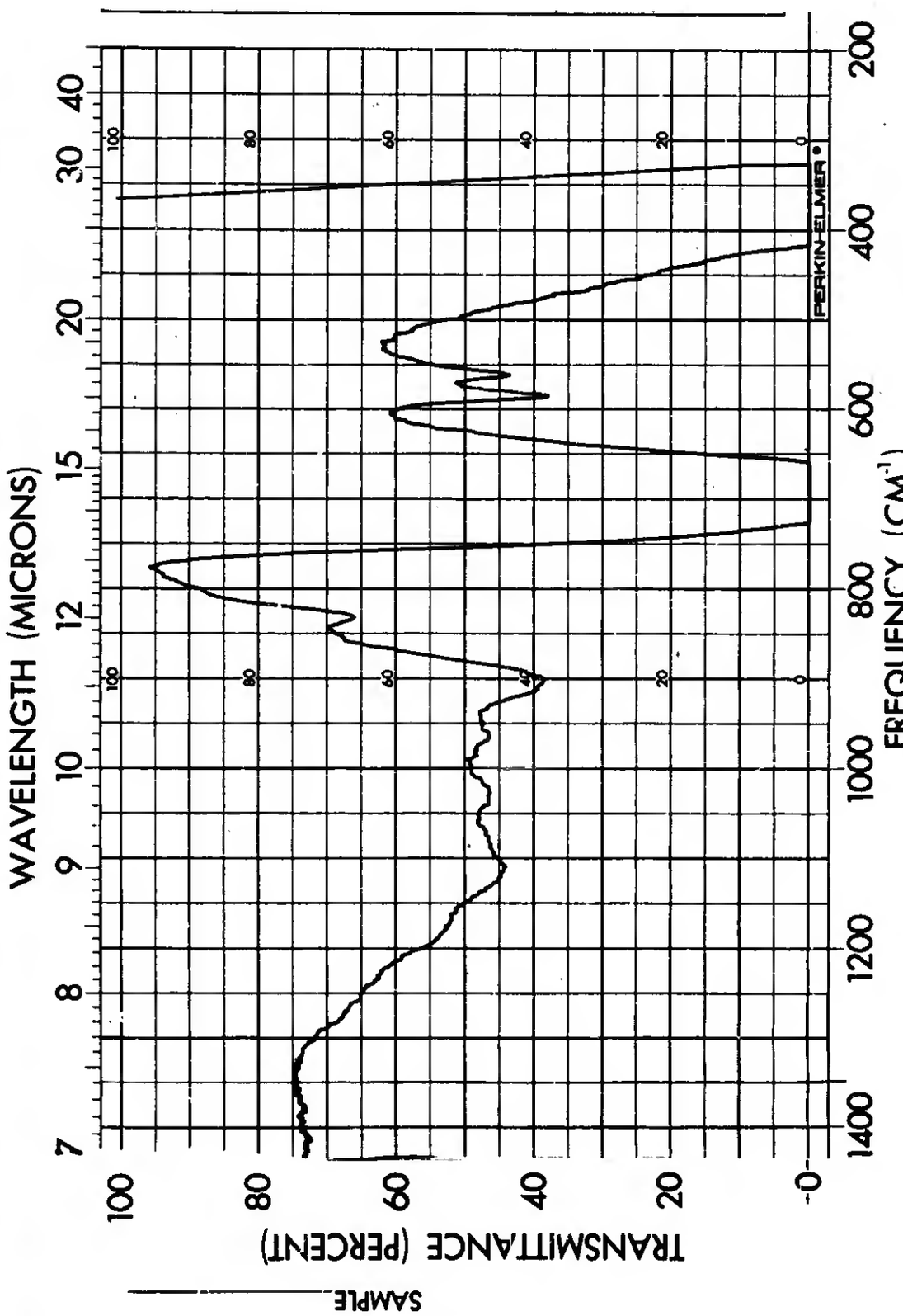


Figure 2. Infrared Spectrum of $N_2F_4(AsF_5)_x$ between -80°C and Room Temperature

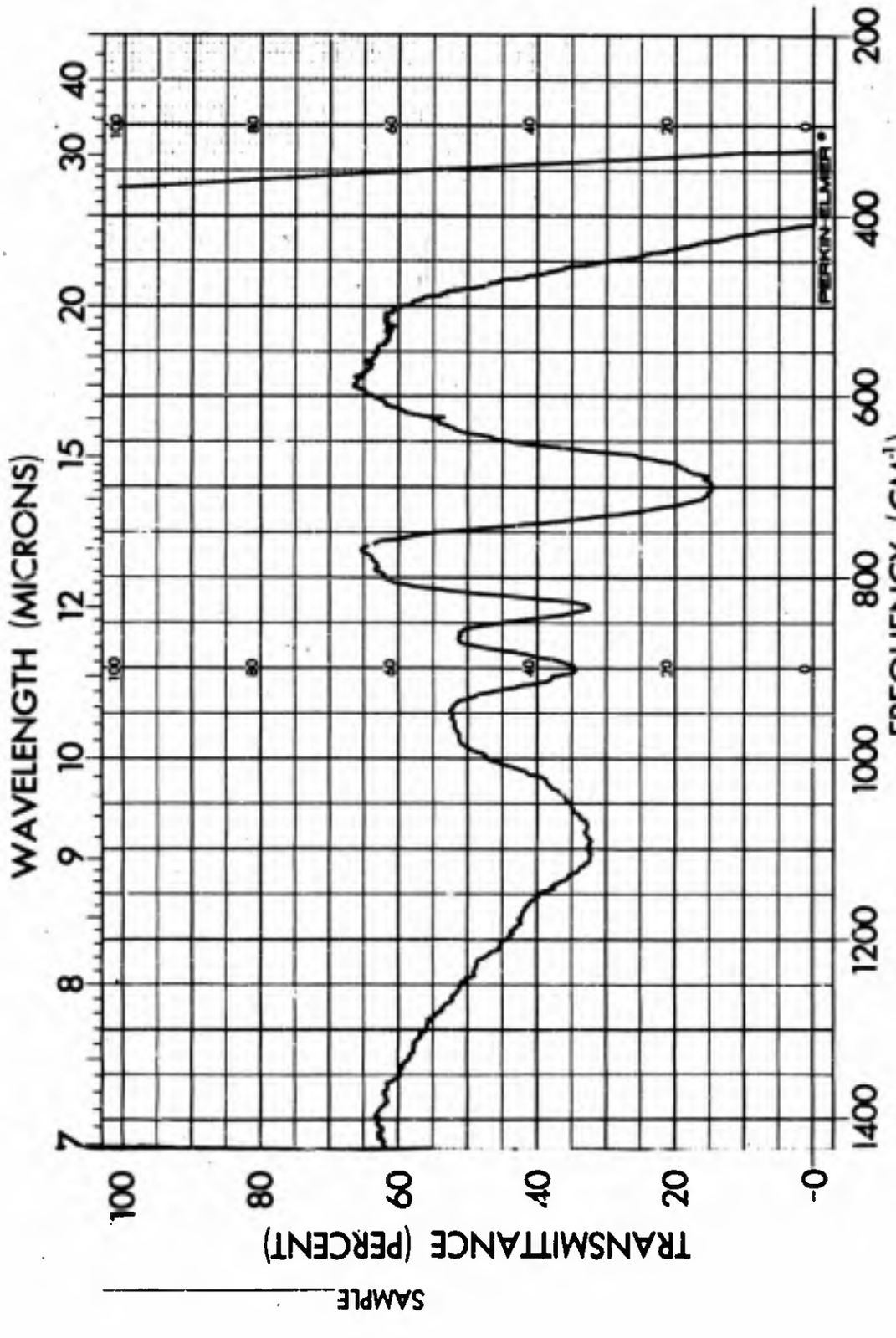
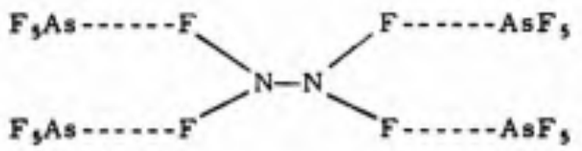


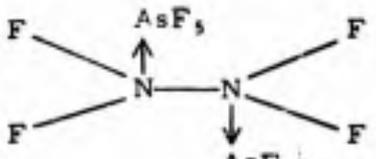
Figure 3. Infrared Spectrum of $N_2F_4 \cdot AsF_5$ at Room Temperature

and the similarity between that spectrum and the one recorded at -80°C bears this out. It should be noted that continued pumping of this adduct at room temperature for several hours was required before the spectrum recorded in Figure 3 was obtained. In method (2), it is possible that some reaction took place between the adduct and SbF_5 to form the material reported by Ruff (Ref 4). This compound has a reported stoichiometry of NF_2SbF_5 at room temperature and is analogous to our product formed at -80°C. The two compounds may have identical N-F species; the similarity between the spectra of the AsF_5 adduct, recorded both at -80°C and in an SbF_5 mull at room temperature, and the spectrum of the SbF_5 adduct, at room temperature, bear this out. Thus it appears that the 1300 cm^{-1} and 940 cm^{-1} bands are associated with the particular N-F structure present in the $N_2F_4(AsF_5)_2$ or $N_2F_4(SbF_5)_2$ compound, while the $N_2F_4 \cdot AsF_5$ adduct exhibits N-F absorptions at 900 cm^{-1} and 830 cm^{-1}. One band, at 1100 cm^{-1}, which may also be an N-F absorption is common to both adducts. A final point of significance is that there appears to be substantial rearrangement in the N-F portion of the adducts as the compositions vary from $N_2F_4(AsF_5)_2$ at -80°C to $N_2F_4 \cdot AsF_5$ at room temperature.

The structures of the adducts are not, as yet, defined. The preparative data consistently show an AsF_5:N_2F_4 ratio greater than 2:1 for the low temperature adduct suggesting that this adduct is formed through fluorine bridge bonding (leading ultimately to I), rather than through nitrogen lone-pair donation (II).



I



II

The infrared spectrum shows a broad absorption at 700 cm^{-1} typical of the AsF_6^- ion, but it is not too unreasonable to expect the As-F vibrations in I to appear in this region. Another possibility, however, is that at low temperatures, the AsF_6^- can associate with AsF_5 yielding $N_2F_3^+ As_2F_{11}^-$. Such a complex anion would be expected to absorb in the region where AsF_6^- is known to absorb.

The room temperature adduct is judged to be ionic (at least in solution) on the basis of its reaction with NaF in IF_5. This produces a mixture of N_2F_4, NF_3 and trans-N_2F_2. A molecular adduct, formed either through fluorine

bridge bonds or nitrogen lone-pair donation should produce N_2F_4 as the only product on displacement of the N-F species by the stronger base, fluoride ion.

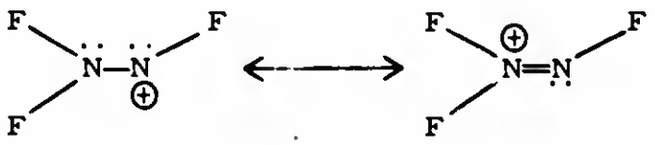
In order to obtain further chemical evidence pointing to an ionic constitution ($N_2F_3^+AsF_6^-$) for the 1:1 adduct, we are presently studying the preparation of the adduct in anhydrous HF. Arsenic pentafluoride is a very strong acid in HF ($AsF_5 + 2HF \longrightarrow H_2F^+ + AsF_6^-$) and there should be no molecular AsF_5 species present in dilute solutions of AsF_5 in HF. Therefore, N_2F_4 will not react with such solutions if the adduct is molecular ($N_2F_4 \cdot AsF_5$). Conversely, if we do obtain an adduct it follows that it must be a hexafluoroarsenate salt ($N_2F_4 + H_2F^+ + AsF_6^- \longrightarrow 2HF + N_2F_3^+ + AsF_6^-$).

Two ionic structures (III and IV) are possible. Structure IV would be more likely to arise at room temperature if the low temperature adduct were formed through nitrogen lone-pair donation (II). Structure III, on the other hand, would be the logical end product of adduct formation through fluorine bridging (I).

$N_2F_3^{\oplus}AsF_6^{\ominus}$ $\qquad$ $NF_2^{\oplus}AsF_5NF_2^{\ominus}$

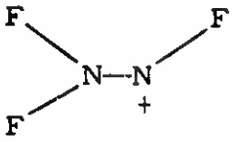
III $\qquad$ IV

The chemistry of the reaction of the adduct with NaF in IF_5 is compatible with either structure III or IV. In III, the ion is probably best represented by a hybrid structure (V) so that F^- attack can occur at either nitrogen (Equations

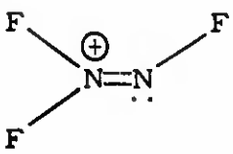


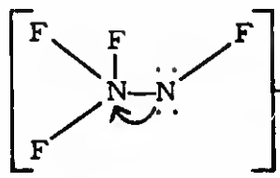
V

3 and 4). From structure IV the same products can arise, but through a much more complex series of reactions (Equations 5-8).



$$+ \; F^{\ominus} \longrightarrow N_2F_4 \qquad (3)$$





$$\longrightarrow NF_3 + 1/2N_2F_2 \qquad (4)$$

$$NF_2^{\oplus} + F^{\ominus} \longrightarrow NF_3 \qquad (5)$$

$$AsF_5NF_2^{\ominus} + Na^{\oplus} \longrightarrow [NaAsF_5NF_2] \longrightarrow NaAsF_6 + 1/2N_2F_2 \qquad (6)$$

$$AsF_5NF_2^{\ominus} + F^{\ominus} \longrightarrow AsF_6^{\ominus} + [NF_2^{\ominus}] \qquad (7)$$

$$NF_2^{\ominus} + NF_2^{\oplus} \longrightarrow N_2F_4 \qquad (8)$$

A clear-cut choice between III and IV is made possible by F^{19} n.m.r. spectroscopy. The F^{19} n.m.r. trace obtained on an HF solution of the adduct was reported previously (Ref 3) and showed three broad peaks at chemical shifts of -134 Ø, -95 Ø, and -67 Ø. We have recently reproduced this spectrum using a freshly prepared solution. The spectrum definitely indicates three distinct N-F absorptions of equal intensity. The values of the chemical shifts have been recalculated on the basis of an assignment of a chemical shift to the "HF" fluorine in the solution relative to Freon-11 by a substitution technique. The revised values for the "NF" fluorines are -180 Ø, -146 Ø, and -122 Ø. We believe that this spectrum definitely rules out structure IV, which should have only two NF absorptions of equal intensity. We further believe that the spectrum is consistent with the presence of an $N_2F_3^+$ cation (structures III and V) in which rotation about the N-N bond is hindered. The absence of free rotation about the N-N bond would make the fluorine atoms nonequivalent thus giving rise to

cis, trans, and gem fluorine-fluorine couplings. Unfortunately, the observed peaks are quite broad (~1000 cycles) and do not show fine structure due to coupling. Better resolution may not be possible in this system because of the quadrupole broadening effect of the nitrogen nuclei.

B. CHEMISTRY OF OXYGEN SUBFLUORIDES AND OF DIOXYGENYL SALTS

The present objective of this phase of the inorganic oxidizer program is to prepare energetic derivatives of the O_2^+ cation. During the preceding quarter (Ref 3), we completed an investigation of the possible synthesis of O_2ClO_4 by the reaction of NO_2ClO_4 with O_2AsF_6. We concluded that the principal reaction occurring in this system was the formation of oxides of chlorine (most probably Cl_2O_6) and NO_2AsF_6 (Equation 9). During this quarter, we have devoted our principal efforts to the attempted synthesis and isolation of O_2ClF_4 and O_2BrF_4. The heat of formation of O_2ClF_4 has been estimated to be -21 kcal/mole (Ref 3).

$$NO_2ClO_4 + O_2AsF_6 \longrightarrow NO_2AsF_6 + \left[O_2ClO_4\right] \longrightarrow xO_2 + ClO_{6-2x} \quad (9)$$

• REACTION OF NO_2 WITH AsF_5

Although we believed the principal reaction of NO_2ClO_4 with O_2AsF_6 to be as shown in Equation 9, the presence of small quantities of ClO_3F in the gaseous products of the reaction and unidentified diffraction lines in the solid reaction products (predominantly NO_2AsF_6) led us to speculate that a side reaction also occurs as shown in Equation 10. We suggested that the presence of the molecular adduct $NO_2 \cdot AsF_5$, which has been reported by Aynsley, et al. (Ref 5),

$$NO_2AsF_6 + \cdot ClO_3 \longrightarrow ClO_3F + NO_2 \cdot AsF_5 \quad (10)$$

might account for the unknown X-ray lines in the product. We attempted to prove this during the present quarter by preparing a pure sample of $NO_2 \cdot AsF_5$ for X-ray analysis. When NO_2 and AsF_5 were mixed at room temperature in an evacuated glass bulb, the formation of a white solid, as reported by Aynsley, et al., was observed, but X-ray examination of the solid indicated that it was $NOAsF_6$ (cubic, a = 8.00 Å, Ref 6). It appears that instead of simple adduct formation we obtained a reaction such as that shown in Equation 11. We are attempting to confirm this by observing the compositions of volatile products of the reaction of NO_2 with AsF_5 at room temperature. We shall also try to determine under what conditions, if any, the molecular adduct $NO_2 \cdot AsF_5$ may be prepared and isolated.

$$2NO_2 + 3AsF_5 \longrightarrow 2NOAsF_6 + O_2 + AsF_3 \qquad (11)$$

- REACTION OF O_2AsF_6 WITH $CsBrF_4$

The reaction of O_2AsF_6 with $CsBrF_4$ might lead to the formation of O_2BrF_4 as shown in Equation 12. This preparation was attempted at room temperature

$$O_2AsF_6 + CsBrF_4 \xrightarrow{?} O_2BrF_4 + CsAsF_6 \qquad (12)$$

in a glass apparatus and in the absence of solvent. Shortly after mixing the two solid reagents, a color change gave evidence of the occurrence of a reaction. The gases evolved during a 45-minute mixing period were F_2, O_2, SiF_4, and Br_2. The presence of SiF_4 and Br_2 suggests that either O_2BrF_4, or its thermal decomposition products, reacts with glass at room temperature. The solid residue was identified as predominantly $CsAsF_6$ by X-ray analysis. Further efforts to prepare O_2BrF_4 will be conducted in a Kel-F system.

- REACTION OF O_2AsF_6 WITH $CsClF_4$

Since lattice energy calculations lead to a ΔH_f value of -21 kcal/mole (Ref 3) for the hypothetical salt, O_2ClF_4, we have initiated attempts to prepare this oxidizer from O_2AsF_6 as shown in Equation 13. Eventually, we may find it

$$O_2AsF_6 + CsClF_4 \longrightarrow O_2ClF_4 + CsAsF_6 \qquad (13)$$

desirable to use a solvent in order to obtain this result, but our initial runs were conducted by mixing the reagents at 0°C in the solid state.

A considerable amount of effort was expended in the preparation of $CsClF_4$ for use in these experiments. This proved to be a very difficult compound to prepare in a reasonable state of purity. We used the method of Whitney, et al. (Ref 7) in which CsF and ClF_3 are combined at 100°C. We identified $CsClF_4$ in the product by comparison of X-ray patterns of our products with X-ray data for $CsClF_4$ supplied by L. B. Asprey (Ref 8).

Unfortunately we do not have the relative intensities of the "d" spacings of $CsClF_4$ observed by Asprey. The strongest lines in our product occur at 3.626, 3.456, 3.342, 3.175, 3.032, and 2.329 Å. Ten of the "d" spacings of this product match those of Asprey fairly well. However, two of the strongest lines, at 3.342 and 3.175 Å, do not correspond to any observed by Asprey for $CsClF_4$. We believe these two lines are due to an impurity since emission spectra of samples of our $CsClF_4$ show the presence of substantial amounts of Cr, Fe, Ni, and Mo. Their presence is due, no doubt, to the attack of liquid ClF_3 at elevated temperature and pressure on the stainless steel bombs used in the preparations. In spite of this obvious contamination of our products, their chemical behavior resembled that reported by Whitney for $CsClF_4$. They reacted violently with water and showed strong oxidizer activity with acidic KI. We found it necessary to remove all traces of HF from the ClF_3 reagent in order to obtain a product of high reactivity. This was done by passing the ClF_3 over NaF at 100°C. We expect to be able to obtain purer samples of $CsClF_4$ in the future by using nickel or Monel reactors.

Two experiments were carried out in which O_2AsF_6 and $CsClF_4$ were mixed together for several hours in a vacuum. The initial experiment was carried out in a glass reactor in the absence of a solvent. We found that in this case a mixture of O_2, F_2, and SiF_4 was evolved, and that $CsAsF_6$ was formed as a solid product. However, the amount of O_2 given off during the reaction was considerably less than the total amount available from the quantity of O_2AsF_6 used. No volatile chlorine compounds were recovered in the products of this reaction. Although unreacted O_2AsF_6 was not detected by X-ray, it, or some other dioxygenyl compound, must have been present in the solid residue.

The other experiment was conducted in a metal, Kel-F apparatus. Analysis of the results is still incomplete. We did, however, discover that Cl_2, as well as O_2, was given off during the reaction. X-ray analysis of the solid product showed that $CsAsF_6$ was the principal constituent, but there were two unidentified "d" lines at 12.54 and 11.33 Å of significant intensity. Further studies of this reaction in the solid state, as well as in the solution, are now in progress.

IV. EXPERIMENTAL

A. PREPARATION OF trans-N_2F_2

The apparatus used in the preparation of trans-N_2F_2 followed the design described by Hurst, et al. (Ref 1). The reactor consisted of a glass U-trap (~250 cc volume) connected to a vacuum line by 18/9 ball joints. In a typical run, 15-18 g. of dry $AlCl_3$ was sublimed onto the walls of the reactor. The reactor was cooled to -80°C and evacuated. One arm of the glass reactor was connected to a storage bulb containing 30-mmole N_2F_4. The bulb was cooled to -135°C in order to maintain a pressure of 15-20 mm. during the run. The other arm of the reactor led to a manometer and a train of collecting traps opened to a vacuum pump. Between the reactor and set of collecting traps was a Teflon needle valve with which the flow of N_2F_4 through the reactor could be controlled.

To initiate the reaction, 15 mm. of N_2F_4 was introduced into the reactor with the needle valve closed and kept in contact with the $AlCl_3$ for 20-30 minutes. After the reaction was initiated, the Teflon needle valve was opened partially to allow a slow leakage of gas out of the reactor. The condensable products, trans-N_2F_2, NF_3, and Cl_2 and any unreacted N_2F_4, were collected at-196°C. Separation of the trans-N_2F_2 was effected by fractionation through -135°C and -196°C baths. Two fractionations gave a sample collected in the -196°C trap which showed no Cl_2 by mass spectral analysis. The -196°C fraction was then left open to a vacuum pump at -196°C to remove the bulk of the NF_3. Final analysis by infrared showed trans-N_2F_2 and less than 1% NF_3; N_2F_4 was not observed. Yields of trans-N_2F_2 were of the order of 10-12 mmoles, or 35-40%, based on the amount of N_2F_4 used.

B. PREPARATION OF cis-N_2F_2

Approximately 10 mmoles of trans-N_2F_2 was distilled into a 500-cc, 316-stainless steel container (≃0.5 atm.) and heated overnight at 75-80°C according to the procedure described by Hurst, et al. (Ref 1). The contents of the cylinder were then cooled to -196°C and the noncondensables pumped off. Infrared analysis of the condensable portion showed cis-N_2F_2 (> 90%), trans-N_2F_2 (< 10%) and NF_3 (trace). The total recovery yield of N_2F_2 was ≃80-90%.

C. TETRAFLUOROHYDRAZINE - ARSENIC PENTAFLUORIDE ADDUCT

1. Preparation and Stoichiometry

In a typical experiment, 5.0 mmoles N_2F_4 and 23.6 mmoles AsF_5 were condensed into a 95-cc Fischer-Porter glass reactor at -196°C. The reactor was warmed to -80°C and kept at that temperature for 18-24 hours. The volatile components at -80°C were then removed and analyzed by infrared spectroscopy and PVT measurements. The reactor was then warmed to ambient temperatures with continual pumping to remove volatiles. Analysis of the volatile fractions was again accomplished by infrared and PVT measurements. The results of these measurements are presented in Table I (Discussion Section).

2. Reaction of $N_2F_4 \cdot AsF_5$ and NaF in IF_5

A Kel-F reactor was loaded with 264 mg of $N_2F_4 \cdot AsF_5$ and excess NaF. Purified IF_5 was distilled into the reactor and the reactor was warmed to ambient temperatures. The reactor was then cooled to -80°C and the volatile components (all condensable at -196°C) were removed. Analyses by PVT and gas chromatography showed 0.88 mmole N_2F_4, 0.05 mmole trans-N_2F_2 and 0.36 mmole NF_3. Total nitrogen was calculated to be 11.9% (calculated for $N_2F_4 \cdot AsF_5$, 10.2%). It appears likely from these results that the volume of the gas measurement apparatus needs to be recalibrated.

3. Infrared Spectra

Infrared spectra were obtained at -80°C and ambient temperature by use of the specially constructed low temperature cell described previously (Ref 2). The cell consisted of an AgCl window cemented into a hollow copper block which could be cooled to the desired temperature. The window and copper block were inserted into a Pyrex gas infrared cell with AgCl windows. The adduct was formed directly on the AgCl plate by condensing N_2F_4 and AsF_5 (10^{-2} mmoles and 4×10^{-2} mmoles, respectively) onto it at -196°C. The copper block was warmed to -80°C and kept at that temperature for several hours. At the end of that time, all volatile components (at -80°C) were removed, leaving behind a thin film deposited on the window. The infrared spectrum from 2 to 25μ was then recorded. The block was allowed to warm slowly to ambient temperatures with continual removal of volatile components and the spectra were recorded at several intervals.

4. F^{19} N.M.R. Spectra

The F^{19} n.m.r. spectra were recorded in HF at ambient temperatures. Approximately 30% solutions were prepared in 5-mm Halon tubes which were fitted to 1/4-in. Swagelok valves using Teflon tape in place of ferrules. The chemical shift of HF was determined to be 169 ±5 Ø using a substitution method. The N-F peaks were determined to be -122 ±5 Ø, -145 ±5 Ø and -180 ±5 Ø from the position of HF side bands.

D. REACTION OF AsF_5 WITH NO_2

A sample of reagent grade NO_2 was allowed to react at room temperature with O_2 to convert the NO impurity to NO_2. Equimolar quantities of NO_2 and AsF_5 were condensed into a glass reactor at -196°C. When the mixture was allowed to warm to room temperature, a white solid was formed. The X-ray powder pattern of the product corresponded to that of $NOAsF_6$ (cubic, a = 8.00 Å).

E. REACTION OF $CsBrF_4$ WITH O_2AsF_6

The $CsBrF_4$ used in this experiment was prepared from CsF and BrF_3 at 100°C and was identified by means of its X-ray diffraction pattern. A 0.52 g. (1.8 mmoles) sample of this material was mixed with 0.34 g. (1.54 mmoles) of O_2AsF_6 in an evacuated glass reactor at room temperature. The solids became brown during the 45-minute reaction period. At the end of this time the reactor was chilled to -78°C, whereupon needle-like red crystals of bromine were observed. At -196°C, 1.97 mmoles of noncondensable gas were present. Of this, 16.4% was F_2 (determined by Hg absorption), with the balance being oxygen. The solid was pumped at -196°C and the vapors over it at -78°C and at 25°C were then examined by mass spectroscopy. Oxygen, SiF_4, CO_2, and fluorocarbon fragments were observed at -78°C, and bromine was observed at room temperature, in addition to the other gases. A sample of the solid residue released no gaseous product upon reaction with water. Its X-ray pattern was essentially identical to a reference pattern for $CsAsF_6$.

F. REACTION OF $CsClF_4$ WITH O_2AsF_6

A 0.95 g. sample of $CsClF_4$ obtained from the reaction of CsF and ClF_3 in a stainless steel bomb at about 110°C was used in this experiment. Although spectrographic analysis of similar preparations of $CsClF_4$ show they

contain considerable amounts of Cr, Fe, Ni, and Mo from the stainless steel bomb, most of the "d" lines of the X-ray pattern of the material agreed fairly well with the reference pattern obtained from Los Alamos laboratories. To this sample of $CsClF_4$ in a glass apparatus was added 0.64 g. (2.9 mmoles) of O_2AsF_6. The mixture was stirred for 3.0 hours at 0°C. A total of 0.9 mmole of gas was given off during this period. This contained approximately 20% F_2, the other components being O_2 and SiF_4. These gases were removed from the reactor and the solid product was allowed to warm to room temperature. An additional 0.426 mmole of gas was then evolved. This was found by mass spectrometric analysis to contain 95% O_2 and 5% SiF_4. The X-ray powder pattern of the solid product showed some of the same "d" lines observed in the original $CsClF_4$ sample, as well as those of $CsAsF_6$.

An additional experiment was conducted to evaluate the reaction of O_2AsF_6 and $CsClF_4$ in a Kel-F reactor. A freshly prepared sample of $CsClF_4$ (0.61 g.) was mixed in a Kel-F reactor at 0°C with 0.48 g. (2 mmoles) of O_2AsF_6. Mixing was continued for three hours. At the end of this time, the mixture was chilled to -78°C and the gases were analyzed. Mass spectrometric analysis of these gases showed that they contained a mixture of O_2 and Cl_2. Quantitative analysis of the gases evolved from the solid product at room temperature is incomplete at this time. X-ray analysis of the brown powder which remained showed unidentified "d" lines at 12.54 and 11.33 Å, but the rest of the pattern corresponded to the pattern calculated for $CsAsF_6$.

IV. FUTURE WORK

1. Characterization studies of $N_2F_4 \cdot AsF_5$ will be continued and further investigation of its chemistry will be conducted.

2. The studies of the chemistry of N_2F^+ salts will be resumed.

3. Attempts to prepare O_2ClF_4 and O_2BrF_4 will be continued.

4. Characterization of the $NO_2^{\oplus}AsF_5$ reaction will be completed.

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Task 51 - The preparation and chemical reactions of organic fluoronitrogen compounds are being investigated. The synthesis of cyclohexylidene-fluorimine and a trifluoroamidine is described.

Several vic- and gem-bis(difluoramino)alkanes were prepared and purified to >99% for the study of structure-sensitivity relationships. (U)

Task 53 - Efforts to characterize arsenic pentafluoride-tetrafluorohydrazine adducts are described. Material balance determinations during the preparation of $N_2F_4(AsF_5)_x$ indicate that x is approximately two at -80° and one at ambient temperatures. Chemical and F^{19} n.m.r. data suggest an ionic constitution ($N_2F_3^+AsF_6^-$) for the room temperature (1:1) adduct. (U)

Task 55 - Thermal decomposition experiments have been performed on hydroxylammonium perchlorate in the temperature range 120°-160°, and the value of the activation energy determined. Preliminary identification of the products has been made, and further experiments designed to extend the study of the stoichiometry of reaction. (U)

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Alkyldifluoramines						
Alkylidenefluorimines						
Sensitivity						
Perchlorates						
Thermal Decomposition						
Hydroxylammonium Perchlorate						
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Thiokol
REACTION MOTORS DIVISION

SECTION III

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W. Cruice

Report RMD 5043-Q2-65

RMD Project 5043, Task 55
Report Period: 1 April 1965
to 30 June 1965

Contract No. NOnr 4364(00)
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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 April 1965 to 30 June 1965 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

ABSTRACT

A method suitable for preparation of research quantities of high-purity hydroxylammonium perchlorate (HAP) in a reasonably short time has been developed. Thermal decomposition rate experiments have been performed in the region of 120°-160° and the activation energy of the uncatalyzed reaction found to be 44.3 kcal/mole. In contrast to the $HONH_3Cl$ reaction previously studied, no evidence of competing reactions is shown.

The vaporous products have been identified as N_2O, HCl and Cl_2; ClO_4^-, $HONH_2$ and NH_3 have been found in the highly acidic condensed residue, which is suspected to be a mixture of HAP, NH_4ClO_4 and aqueous $HClO_4$. Experiments designed to discover the stoichiometry of the reaction have been undertaken.

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I. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy solid oxidizers in order to understand the mechanism by which they decompose. Work previously reported includes a detailed literature search, results of experimental work on the vapor pressure and thermal decomposition of anhydrous perchloric acid, determination of the temperature coefficients and stoichiometry of the reaction of hydrazinium perchlorate, determination of the temperature coefficients of the reaction of hydroxylammonium chloride, results of studies to date on hydroxylammonium perchlorate, and results of preliminary experiments on hydrazinium diperchlorate.

Additional batches of hydroxylammonium perchlorate have been synthesized and additional thermal decomposition experiments have been performed. A new quantity of high-purity hydrazinium diperchlorate has been prepared for thermal decomposition experiments.

This report includes a summary of experimental work done in the second quarter of 1965 and a brief outline of projected work for the following quarter.

II. SUMMARY

During this report period a method suitable for preparation of research quantities of high-purity hydroxylammonium perchlorate (HAP) in a reasonably short time has been developed. Thermal decomposition rate experiments have been performed in the region of 120°C-160°C and the activation energy of the uncatalyzed reaction found to be 44.3 kcal/mole. In contrast to the $HONH_3Cl$ reaction previously studied, no evidence of competing reactions is shown.

The vaporous products have been identified as N_2O, HCl and Cl_2; ClO_4^-, $HONH_2$ and NH_3 have been found in the highly acidic condensed residue, which is suspected to be a mixture of HAP, NH_4ClO_4 and aqueous $HClO_4$. Experiments designed to discover the stoichiometry of the reaction have been undertaken.

III. EXPERIMENTAL

A. PROCEDURES

1. Rate Experiments

The methods used in these experiments have been discussed in detail in Reference 1.

2. Stoichiometry Experiments

The basic apparatus, illustrated schematically in Figure 1, is composed of three units. The reactor is a spherical vessel with an exit path for gaseous decomposition products provided through a needle valve at the top. The second chamber, a U-trap with needle valves at either end, is maintained at -78°C in these experiments. The third unit, a trap of the usual design, is maintained at -196°C. Kel-F 90 grease is used on the ball joint connections from unit to unit; some reaction with the products of the decomposition have been observed, but so slight an amount as to be of no major consequence.

In a typical experiment, about 1.5 g. of HAP is placed in the reactor in a dry box, the reactor is connected to the traps, and the entire system evacuated at 0.05 mm. Hg. pressure for 30-60 min. at ambient temperature. The oil bath (at 150°C) is raised around the reactor, and the -78°C and -196°C baths raised around the traps. The reaction is allowed to proceed for approximately 5 hours. The shutdown procedure is quite similar; after the oil bath is lowered, the valve on the reactor is shut, and any condensate in the connecting arm is vaporized with a heat gun. The valves are then closed in order, proceeding from the reactor to the -196°C outlet, and the cold baths removed.

The reactor unit is weighed, the contents dissolved in H_2O, and the reactor dried and reweighed. The acid equivalency of the contents is determined by potentiometric titration with NaOH solution, and qualitative and quantitative tests for $HONH_2$, ClO_4^-, NH_3, Cl^- are performed. The pressure of the contents of the -196°C trap is determined in a calibrated volume, the contents recondensed and subsequently re-expanded into an infrared spectrophotometer cell for identification. The contents of the -78°C trap are treated

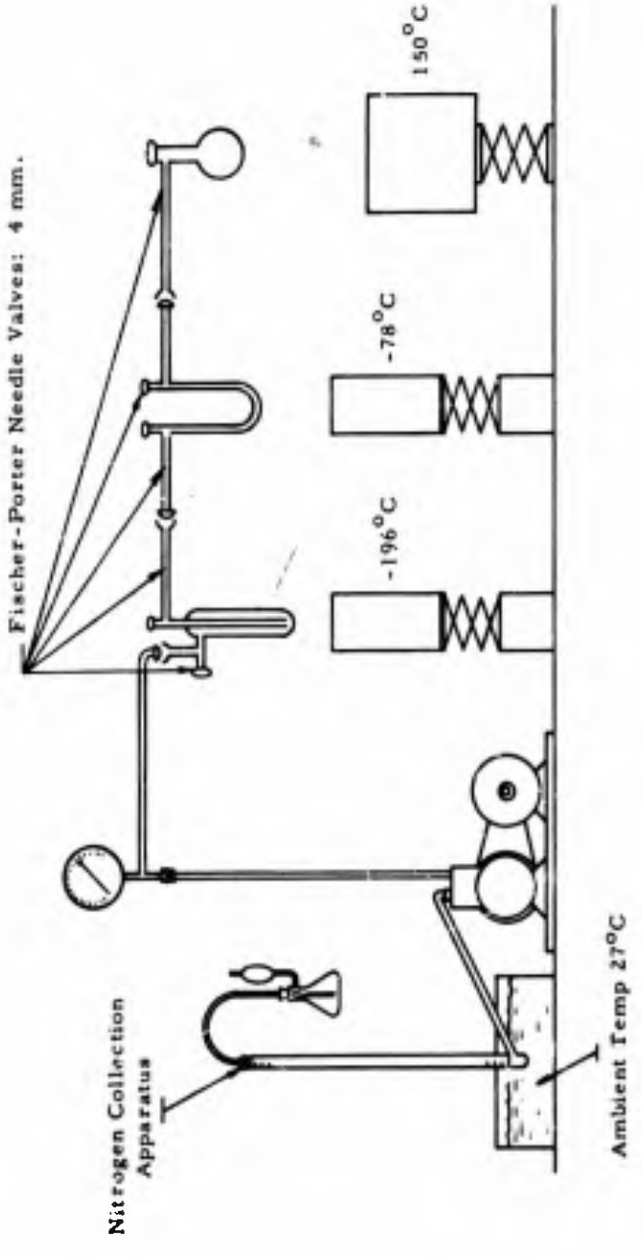

Figure 1. Stoichiometry Experiments: Apparatus

according to both procedures, identification of the vapors (at ambient temperature) first and wet analysis of the condensate afterwards.

An attempt was made to trap N_2 and O_2 (if any) generated in the decomposition in a gas burette system as included in the illustration; a leak in the intermediate lines has rendered this effort fruitless to date.

B. MATERIALS

1. Hydroxylammonium Perchlorate (HAP)

The method of production of HAP described previously (Ref 2) results in a reasonably pure product, but the lengthy oven drying process is subject to several possible difficulties. A further simplification of this method has been developed which yields HAP of excellent quality in a much briefer period in sufficient quantities for our purposes.

Stoichiometric amounts of $Ba(ClO_4)_2$ and $HONH_3Cl$ are dissolved in absolute ethanol and the two solutions mixed. $BaCl_2$ precipitates and is filtered out, and the ethanol removed in a flash evaporator. The solid HAP is dissolved in anhydrous diethyl ether and any residue filtered out; the ether is then evaporated. This purification is repeated until no residue is detected, at which point the HAP is precipitated from the solution with benzene. This material is dried in a glass dead-end tube for approximately one hour at 70°C and 0.05 mm. Hg., at which point it was assayed as ~97% pure. The tube is closed and the material stored in this form in a dry box. When a sample is required, the appropriate amount of material is removed and redissolved in ether, then reprecipitated with benzene and dried for one hour at 70°C and 0.05 mm. Hg. as before.

Samples prepared in this manner consistently assay well in excess of 99% purity, and the drying time is cut by a factor of 12 over that required formerly. Spot tests for Cl^- are regularly negative, quantitative tests for ClO_4^- and $HONH_2$ are not yet complete.

IV. RESULTS AND DISCUSSION

A. RATE EXPERIMENTS

The amount of gaseous products per mole of starting material has been monitored as a function of time in the temperature range 120°C-160°C. The data are reproduced in Table I and illustrated in Figure 2. There is some scatter in the actual experimental plots, but data for different temperatures fall into very easily definable zones on the composite plot. The illustrated curves are therefore average plots for four or more experiments at each temperature, except at 120°C, where only one experiment is completed. Results of mass spectrometric analysis of residual vapors at ambient temperature are included in the table.

Despite the scatter previously mentioned, the precise curves for all these reactions exhibit certain common characteristics. At first the slope is low; then a brief increase and subsequent decrease in slope give an inflection. (This inflection occurs in all cases, but the time and the n/N_o value is not the same in all cases.) The slope then increases somewhat to achieve a constant value for a rather considerable period, after which a gradual increase is observed for the druation of the experiment. The linear portion of the curve is usually quite distinct and the slope of this portion has been taken as representative of the rate of normal decompsotion. The subsequent acceleration in the reaction is presumed to represent either catalysis of the reaction by accumulated perchoric acid, independent decomposition of accumulated perchloric acid, or both. The slope of the linear portion of the curve has been graphed versus reciprocal absolute temperature (Figure 3). The activation energy is 44.3 kcal/mole; in contrast to the decomposition of $HONH_3Cl$ (Ref 2), no evidence of competing reactions is indicated in this case.

The absence of competing reactions is also clearly indicated by the analysis of the residual vapors. The principal product and the only nitrogenous product is N_2O; HCl and Cl_2 are the only chlorine-containing products. There is no precise regularity to the proportions of N_2O:HCl:Cl_2; the final readings of n/N_o at elevated temperatures are all different, however, which may account for the difference in HCl and Cl_2 content. Independent decomposition of the

TABLE I

RATE OF DECOMPOSITION OF HYDROXYLAMMONIUM PERCHLORATE AS A FUNCTION OF TEMPERATURE

Run No.	Temperature (°C)	Slope of Linear Portion $\left(\frac{\text{moles of gas}}{\text{moles of HAP} \times \text{min.}}\right)$	Analysis of Residual Vapors at Ambient Temperature (Mole %)				
			N_2O	HCl	Cl_2	N_2	Others
19	130	3.43×10^{-4}	80	17	---	1	2 (NO)
20	130	2.67×10^{-4}	75	25	---	---	---
21	140	11.1×10^{-4}	74	26	---	---	---
22	130	2.90×10^{-4}	85	15	---	---	---
23	140	11.9×10^{-4}	92	8	---	---	---
24	140	14.6×10^{-4}	68	18	14	---	---
25	130	No data	68	25	7	---	---
26	140	11.4×10^{-4}	69	27	4	---	---
27	130	1.73×10^{-4}	82	17	1	---	---
28	140	15.1×10^{-4}	65	31	4	---	---
29	150	43.8×10^{-4}	89	4	7	---	---
30	150	31.4×10^{-4}	← No data →				
31	150	48.3×10^{-4}	67	20	13	---	---
32	150	31.3×10^{-4}	70	19	11	---	---
33	120	No data	66	21	13	---	---
35	120	0.74×10^{-4}	No data as of this writing				

Average Slopes

$120^{\circ}C = 0.74 \times 10^{-4}$
$130^{\circ}C = 2.68 \times 10^{-4}$
$140^{\circ}C = 12.8 \times 10^{-4}$
$150^{\circ}C = 38.7 \times 10^{-4}$

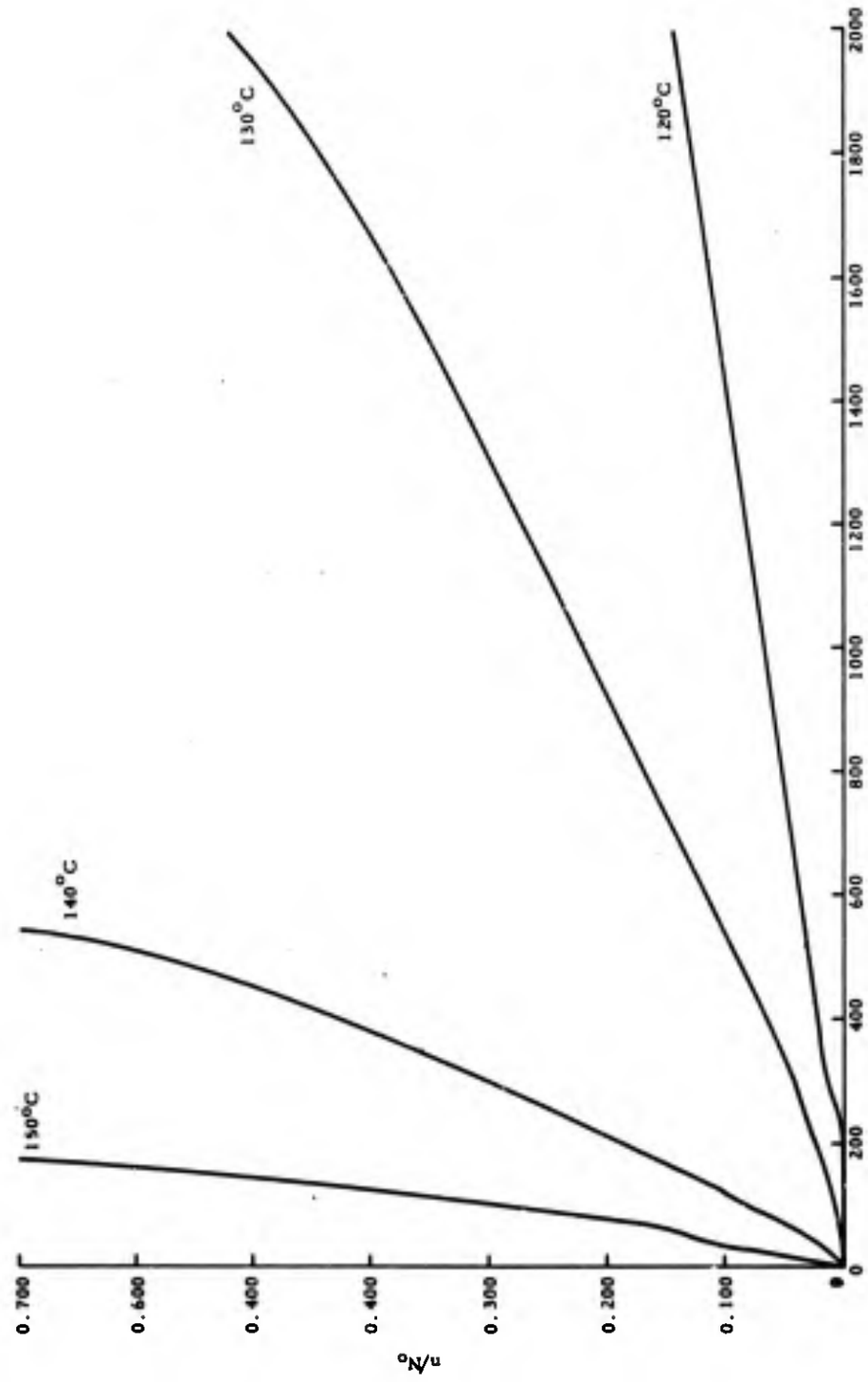

Figure 2. Rate of Decomposition of Hydroxylammonium Perchlorate as a Function of Temperature

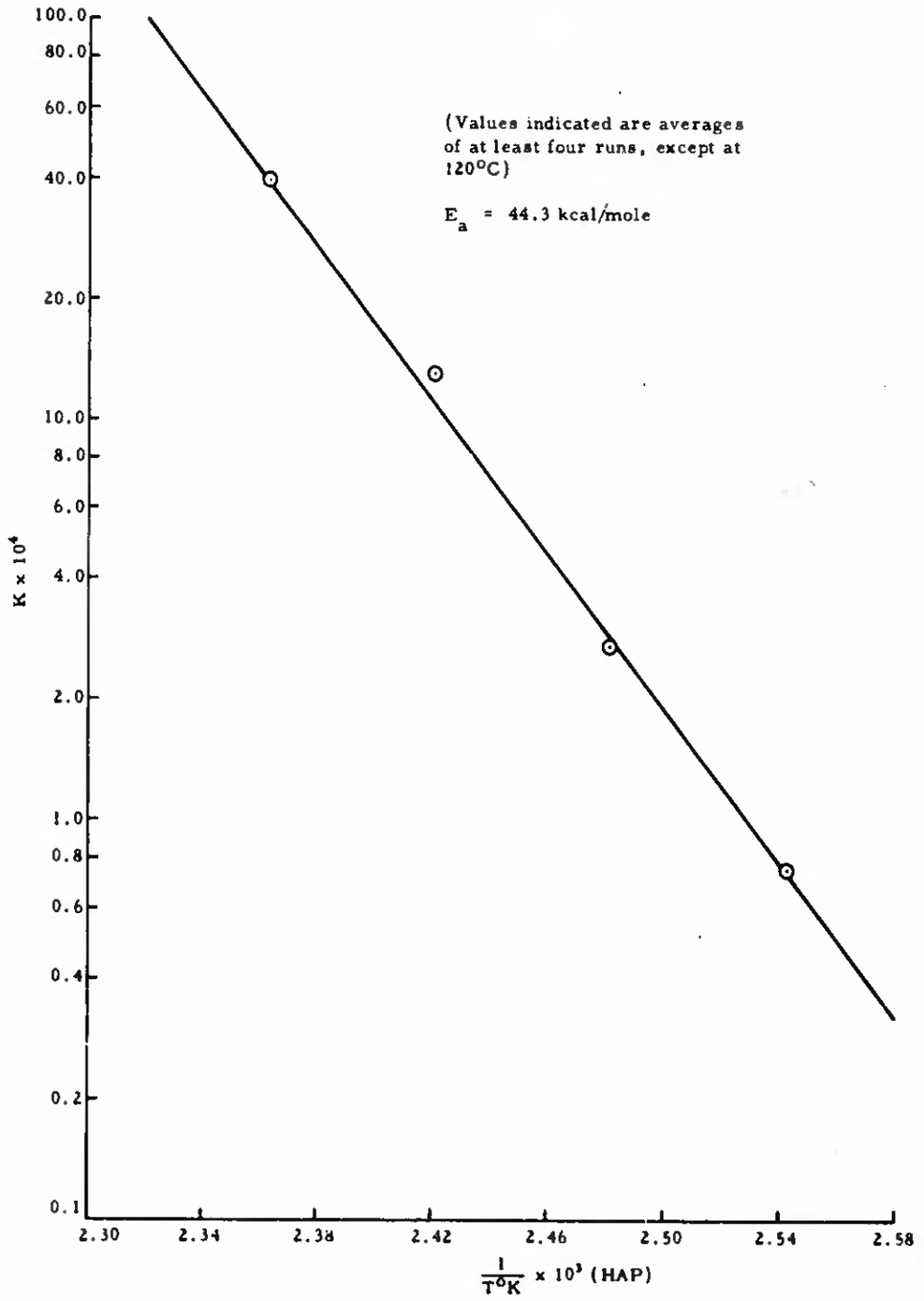

Figure 3. Arrhenius Plot: Coefficient of Linear Portion of Curve vs $\frac{1}{T^{\circ}K} \times 10^{3}$ (HAP)

acid, catalysis of the decomposition by the acid, and the relative degree of each process would be expected to cause differences of this type.

Experiments were also performed at 160°C, but the reaction proceeds too rapidly to be monitored in the usual manner. Decomposition vapors have been contained, however, and are awaiting analysis. The same situation was experienced at 155°C; extension of these investigations will require further effort.

B. STOICHIOMETRY EXPERIMENTS

Experiments using the procedure described above have been started during this period. As mentioned, approximately 1.5 g. of material is maintained at 150°C for approximately five hours, during which period the volatile products are condensed in a series of two traps maintained at -78°C and -196°C. The initial runs performed have been largely of a qualitative and exploratory nature. The contents of the -196°C trap was identified as N_2O; the contents of the -78°C trap were nonvolatile at ambient temperature and gave a strongly acidic solution in 50-100 ml. H_2O. The residue in the reaction vessel was quite acidic but potentiometric titration with NaOH on an automatic titrator indicated a mixture of salts of strong acids and weak bases, as opposed to free acids. The mass of material remaining in the reaction vessel accounted for 81.5% by weight of the starting material.

C. GENERAL DISCUSSION

The n/N_o versus time curves for the experiments performed during this quarter show considerable similarity to those preliminary results recorded previously (Ref 1) and radical difference from those few experiments recorded in the last quarterly report (Ref 2). The "inflection points" of the curves most recently obtained occur at somewhat lower values of n/N_o than the inflection points of those obtained in the preliminary runs. There seems to be a direct correlation between temperature and n/N_o value at inflection. The significance of the inflection in the curve is unknown; it could result from a small amount of impurity vaporizing or decomposing. However, the presence of a similar pattern in the rate curves for thermal decomposition of hydroxylammonium hydrochloride suggests that this characteristic is related to the nature of the salt, rather than to the presence of any impurities.

The radical difference between the curves reported in the last quarterly and those reported here is somewhat of a puzzle. Those reported in the last quarterly would appear to be the result of contamination of the HAP with some

sort of highly catalytic material. In an effort to obtain high-purity material, the preparation employed at that time included drying at 70°C for a period of 24 hours. A sample of relatively low purity (~97%) maintained at 70°C for a considerable period developed pressure at a moderately high rate even in the early stages. It is possible therefore that some decomposition had taken place in the drying process and some highly reactive products were produced which were in sufficient quantity to initiate a more rapid reaction than is normally experienced. This matter is yet to be resolved.

V. FUTURE WORK

Additional information has become available in the literature concerning anhydrous perchloric acid (Ref 3) and hydroxylammonium perchlorate (Ref 4) which has not yet been fully evaluated. Results of mass spectrometer experiments on HAP in Reference 4 are of considerable interest; this information must be examined and correlated with our present work in the near future.

Other work planned as of this writing includes:

- Extension of HAP rate measurements to lower and higher temperatures
- Continuation of stoichiometry experiments on HAP
- Further exploratory experiments on HP-2.

VI. REFERENCES

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